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### PHILOSOPHICAL

# TRANSACTIONS

OF THE

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### SERIES A.

CONTAINING PAPERS OF A MATHEMATICAL OR PHYSICAL CHARACTER.

VOL. 217.



#### LONDON:

PRINTED BY HARRISON AND SONS, ST. MARTIN'S LANE, W.C., Printers in Ordinary to Jis Majesty.

DECEMBER, 1918.



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### ADVERTISEMENT.

The Committee appointed by the Royal Society to direct the publication of the Philosophical Transactions take this opportunity to acquaint the public that it fully appears, as well from the Council-books and Journals of the Society as from repeated declarations which have been made in several former Transactions, that the printing of them was always, from time to time, the single act of the respective Secretaries till the Forty-seventh Volume; the Society, as a Body, never interesting themselves any further in their publication than by occasionally recor nending the revival of them to some of their Secretaries, when, from the particular circumstances of their affairs, the Transactions had happened for any length of time to be intermitted. And this seems principally to have been done with a view to sat just the public that their usual meetings were then continued, for the improvement of knowledge and benefit of mankind: the great ends of their first institution by the Royal Charters, and which they have ever since steadily pursued.

But the Society being of late years greatly enlarged, and their communications more numerous, it was thought advisable that a Committee of their members should be appointed to reconsider the papers read before them, and select out of them such as they should judge most proper for publication in the future *Transactions*; which was accordingly done upon the 26th of March, 1752. And the grounds of their choice are, and will continue to be, the importance and singularity of the subjects, or the advantageous manner of treating them: without pretending to answer for the certainty of the facts, or propriety of the reasonings contained in the several papers so published, which must still rest on the credit or judgment of their respective authors.

It is likewise necessary on this occasion to remark, that it is an established rule of the Society, to which they will always adhere, never to give their opinion, as a Body, upon any subject, either of Nature or Art, that comes before them. And therefore the thanks, which are frequently proposed from the Chair, to be given to the authors of such papers as are read at their accustomed meetings, or to the persons through whose hands they received them, are to be considered in no other light than as a matter of civility, in return for the respect shown to the Society by those communications. The like also is to be said with regard to the several projects, inventions, and curiosities of various kinds, which are often exhibited to the Society; the authors whereof, or those who exhibit them, frequently take the liberty to report, and even to certify in the public newspapers, that they have met with the highest applause and approbation. And therefore it is hoped that no regard will hereafter be paid to such reports and public notices; which in some instances have been too lightly credited, to the dishonour of the Society.

### PHILOSOPHICAL TRANSACTIONS

OF THE

### ROYAL SOCIETY OF LONDON.

SERIES A, VOL. 217. TITLE, &c.

## TITLE, CONTENTS, INDEX, &c.

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PRINTED AND PUBLISHED FOR THE ROYAL SOCIETY BY
HARRISON AND SONS, 44-47, ST. MARTIN'S LANE, LONDON, W.C. 2,

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1918.

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SERIES A, Vol. 217. Pp. 1-34.



# ON THE INSTABILITY OF THE PEAR-SHAPED FIGURE OF EQUILIBRIUM OF A ROTATING MASS OF LIQUID.

BY

J. H. JEANS, M.A., F.R.S.

#### LONDON:

PUBLISHED BY THE ROYAL SOCIETY,

AND SOLD BY HARRISON AND SONS, ST. MARTIN'S LANE, W.C.,

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1916.

A 549.

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### PHILOSOPHICAL TRANSACTIONS.

I. On the Instability of the Pear-shaped Figure of Equilibrium of a Rotating Mass of Liquid.

By J. H. Jeans, M.A., F.R.S.

Received March 21,—Read April 6, 1916.

1. The main result obtained in this paper is sufficiently indicated by its title. In a recent paper\* I showed that the stability of the pear-shaped figure could only be decided on after the figure itself had been calculated as far as terms involving the cube of the parameter e, which is used to measure the deviation of the pear-shaped figure from the critical Jacobian ellipsoid. In the present paper these third-order terms are calculated, and the pear-shaped figure is definitely shown to be unstable.

A statement of the results obtained, and a discussion of their bearing on the wider question of which this problem forms a part, will be found at the end of the paper (§§ 23–27).

2. The discussion has to begin with a determination of the potential of a distorted ellipsoid, carried as far as the third order of the small quantities involved. With a view to shortening very lengthy computations, it is convenient to arrange the algebraic solution in a form somewhat different from that previously given. The solution now given can readily be extended to any order of small quantities, and appears to lead to the most concise series of computations for terms of all degrees above the second.

Potential of a Distorted Ellipsoid carried to the Terms of Third and Higher Orders.

3. As before, the undisturbed ellipsoid (which will ultimately be supposed to be the critical Jacobian) is taken to be the surface  $\lambda = 0$  in the family of surfaces

$$f \equiv \frac{x^2}{a^2 + \lambda} + \frac{y^2}{b^2 + \lambda} + \frac{z^2}{c^2 + \lambda} - 1 = 0, \quad . \quad . \quad . \quad . \quad (1)$$

while the disturbed ellipsoid whose potential we require (which will ultimately be

\* "On the Potential of Ellipsoidal Bodies, and the Figures of Equilibrium of Rotating Liquid Masses," 'Phil. Trans., 'A, vol. 215, p. 27.

supposed to be the pear-shaped figure) is taken to be the surface  $\lambda = 0$  in the more general family,

$$f + \phi \equiv \frac{x^2}{a^2 + \lambda} + \frac{y^2}{b^2 + \lambda} + \frac{z^2}{c^2 + \lambda} + \phi - 1 = 0. \quad . \quad . \quad . \quad . \quad (2)$$

Here  $\phi$  is a function of x, y, z, and  $\lambda$ , different values for  $\phi$  representing different distortions of the fundamental ellipsoid.

If  $V_i$ ,  $V_0$  are the internal and external potentials at x, y, z (or their analytical continuations as explained in the previous paper, § 3), we have seen that  $V_i$ ,  $V_0$  must be of the form

where

$$\psi(\lambda) = -\frac{\pi \rho abc}{\{(a^2 + \lambda)(b^2 + \lambda)(c^2 + \lambda)\}^{1/2}} = -\frac{\pi \rho abc}{\Delta}. \qquad (5)$$

In these integrations, x, y, z are treated as constants while  $\lambda'$  is the value of  $\lambda$  at the point x, y, z as determined by equation (2). Furthermore,  $\phi$  must not be selected at random; equations (3) and (4) will only give the true potentials if  $\phi$  is chosen so as to satisfy

$$-\left(\frac{\partial f}{\partial \lambda} + \frac{\partial \phi}{\partial \lambda}\right) \int_{0}^{\lambda'} \psi(\lambda) \nabla^{2} \phi \, d\lambda + \psi(\lambda) \left[4\Sigma \frac{x}{\Lambda} \frac{\partial \phi}{\partial x} + 4 \frac{\partial \phi}{\partial \lambda} + \Sigma \left(\frac{\partial \phi}{\partial x}\right)^{2}\right] = 0. \quad . \quad (6)$$

This equation, as before, is most conveniently solved by a solution

in which u, v must satisfy the equations

$$4(1+v)\left[\left(\sum \frac{x}{A}\frac{\partial u}{\partial x} + \frac{\partial u}{\partial \lambda}\right) + f\left(\sum \frac{x}{A}\frac{\partial v}{\partial x} + \frac{\partial v}{\partial \lambda}\right)\right] + \sum \left(\frac{\partial u}{\partial x} + f\frac{\partial v}{\partial x}\right)^2 = 0. \quad . \quad (9)$$

4. We attack the second equation first. As in the previous paper, let us introduce new co-ordinates  $\xi$ ,  $\eta$ ,  $\xi$  defined by

$$\xi = \frac{x}{a^2 + \lambda} = \frac{x}{A}, \&c.,$$

and the equation is found to reduce to (cf. equation (37) of the previous paper)

$$4 \left( 1 + v \right) \left( \frac{\partial u}{\partial \lambda} + f \frac{\partial v}{\partial \lambda} \right) + \sum \frac{1}{A^2} \left( \frac{\partial u}{\partial \xi} + f \frac{\partial v}{\partial \xi} \right)^2 = 0.$$

In this equation we may put  $f+\phi=0$ , or, since  $\phi=u+fv$ , we may put

$$f = -\frac{u}{1+v},$$

although of course it would not be legitimate to equate differential coefficients of these equal quantities. The equation reduces to

$$4\frac{\partial}{\partial\lambda}\left(\frac{u}{1+v}\right) + \Sigma\left[\frac{\partial}{\partial\xi}\left(\frac{u}{1+v}\right)\right]^2 = 0, \quad . \quad . \quad . \quad . \quad (10)$$

and this may be readily solved in powers of the parameter e on assuming a series of the form

$$\frac{u}{1+v} = eg_1 + e^2g_2 + e^3g_3 + e^4g_4 + \dots (11)$$

Equating coefficients of the different powers of c we obtain

$$\begin{split} \frac{\partial g_1}{\partial \lambda} &= 0, \\ \frac{\partial g_2}{\partial \lambda} &= -\frac{1}{4} \Sigma \frac{1}{\mathbf{A}^2} \left( \frac{\partial g_1}{\partial \xi} \right)^2, \\ \frac{\partial g_3}{\partial \lambda} &= -\frac{1}{4} \Sigma \frac{1}{\mathbf{A}^2} \left( 2 \frac{\partial g_1}{\partial \xi} \frac{\partial g_2}{\partial \xi} \right), \text{ and so on.} \end{split}$$

To satisfy the first of these equations,  $g_1$  must be a function of  $\xi$ ,  $\eta$ ,  $\zeta$  only, say P. To satisfy the remaining equations, write

$$\mathbf{A} = \frac{1}{\alpha^2} - \frac{1}{\mathbf{A}}$$
, &c., so that  $\frac{\partial \mathbf{A}}{\partial \lambda} = \frac{1}{\mathbf{A}^2}$ , &c.

Then if  $P_{\xi}$  is written for  $\partial P/\partial \xi$ , the equation for  $g_2$  is

$$\frac{\partial g_2}{\partial \lambda} = -\frac{1}{4} \sum \frac{\partial \mathbf{A}}{\partial \lambda} \, \mathbf{P}_{\xi}^2,$$

of which the solution is

$$g_2 = -\frac{1}{4} (\mathbf{A} \mathbf{P}_{\xi}^2 + \mathbf{B} \mathbf{P}_{\eta}^2 + \mathbf{C} \mathbf{P}_{\zeta}^2) + \mathbf{Q}, \quad . \quad . \quad . \quad . \quad (12)$$

where Q is a function of  $\hat{\xi}$ ,  $\eta$ ,  $\xi$  only. Proceeding in the same way, we find

$$g_3 = \frac{1}{8} (\mathbf{A}^2 P_{\xi}^2 P_{\xi\xi} + \dots + 2\mathbf{BC} P_{\eta} P_{\xi} P_{\eta\xi} + \dots) - \frac{1}{2} (\mathbf{A} P_{\xi} Q_{\xi} + \dots) + \mathbf{R}. \quad . \quad (13)$$

where R is another function of  $\xi$ ,  $\eta$ ,  $\xi$  only, and so on.

5. We now return to equation (8). By a transformation given in the previous paper (p. 37), it is found that this is satisfied by taking

$$v = 0$$
 when  $\lambda = 0, \dots$  (14)

and

$$\nabla^2 u + f \nabla^2 v + 4 \left[ \sum \frac{x}{A} \frac{\partial v}{\partial x} + \frac{\partial v}{\partial \lambda} \right] \equiv \Delta \frac{\partial \sigma}{\partial \lambda}, \qquad (15)$$

where  $\sigma$  may be any function of x, y, z and  $\lambda$ , which vanishes when  $\lambda = 0$  and when  $\lambda = \lambda'$ . For equation (15) we may try provisionally a solution

$$v = w + fw' + f^2w'' + \dots + f^n w_n + \dots$$
 (16)

where w, w', w'' ... are quantities satisfying

$$4\left(\Sigma \frac{x}{A} \frac{\partial w}{\partial x} + \frac{\partial w}{\partial \lambda}\right) = -\nabla^2 u - \Delta \frac{\partial \theta}{\partial \lambda}. \qquad (17)$$

$$4\left(\sum \frac{x}{A} \frac{\partial w'}{\partial x} + \frac{\partial w'}{\partial \lambda}\right) = -\frac{1}{2}\nabla^2 w, \dots \qquad (18)$$

$$4\left(\sum \frac{x}{A} \frac{\partial w_n}{\partial x} + \frac{\partial w_n}{\partial \lambda}\right) = -\frac{1}{n+1} \nabla^2 w_{n-1}, \&c. . . . . . (19)$$

After a good deal of simplification, the left-hand member of equation (15) is found to reduce to

$$\nabla^2 u + f \nabla^2 v + 4 \left( \sum \frac{x}{A} \frac{\partial v}{\partial x} + \frac{\partial v}{\partial \lambda} \right) = -\Delta \frac{\partial}{\partial \lambda} \left[ \theta + \frac{4}{\Delta} \left( f w' + 2 f^2 w'' + \dots + n f^n w_n + \dots \right) \right]. \tag{20}$$

The quantity  $\theta$  is so far undetermined. Let it be given by

$$\theta = \frac{4}{\Delta} \left( \frac{u}{1+v} \right) (w' + 2fw'' + \dots + nf^{n-1}w_n + \dots), \quad (21)$$

so that the quantity in the square bracket on the right of equation (20) becomes

$$\left[\frac{4}{\Delta}\left(f + \frac{u}{1+v}\right)\left(w' + 2fw'' + \dots + nf^{n-1}w_n + \dots\right)\right]. \qquad (22)$$

When  $\lambda = \lambda'$ , this vanishes through the factor  $f + \frac{u}{1+v}$ . It will vanish when  $\lambda = 0$  through the last factor if we make

$$w' = w'' = w''' = \dots = 0$$
, when  $\lambda = 0...$  (23)

If this last condition is satisfied, expression (22) satisfies completely the conditions which have to be satisfied by  $\sigma$  in equation (15). Hence the value of v given by

equation (16) will be a solution of equation (15). Moreover, if w', w'', w''' ... all vanish when  $\lambda = 0$ , v will also vanish when  $\lambda = 0$ , so that equation (14) will also be It follows that equations (16) to (19), with (23), contain a complete solution of equation (8).

6. These equations can be solved in powers of the parameter e. Let us assume for u, v expansions in the form

$$u = eu_1 + e^2 u_2 + e^3 u_3 + e^4 u_4 + \dots,$$
  
$$v = ev_1 + e^2 v_2 + e^3 v_2 + e^4 v_4 + \dots.$$

and for  $w, w', w'', \dots$  &c., expansions

$$w = ew_1 + e^2w_2 + e^3w_3 + e^4w_4 + \dots,$$
  
$$w' = ew'_1 + e^2w'_2 + e^3w'_3 + e^4w'_4 + \dots,$$

The coefficients in the expansions of u, v are of course not independent of those in the expansion (11) already assumed for u/(1+v). We find easily enough the relations

$$u_1 = g_1 = P,$$
  
 $u_2 = g_2 + v_1 g_1,$   
 $u_3 = g_3 + v_1 g_2 + v_2 g_1,$   
 $u_4 = g_4 + v_1 g_3 + v_2 g_2 + v_3 g_1,$  &c.

The value of  $\theta$  (equation (21)) is found to be

$$\theta = \frac{4}{\Delta} \left[ e^2 g_1 \left( w'_1 + 2f w''_1 + 3f^2 w'''_1 + \dots \right) + e^3 \left\{ g_2 \left( w'_1 + 2f w''_1 + 3f^2 w'''_1 + \dots \right) + g_1 \left( w'_2 + 2f w''_2 + \dots \right) \right\} \right].$$

On equating coefficients of different powers of e in equations (17)–(19), we obtain

$$4\left(\sum \frac{x}{A} \frac{\partial w'_1}{\partial x} + \frac{\partial w'_1}{\partial \lambda}\right) = -\frac{1}{2}\nabla^2 w_1, \&c., \qquad (25)$$

There are an infinite number of such sets of equations, of which we shall need only the set for  $w_3, w'_3, \ldots$  in addition to the two sets above. To simplify the equations as much as possible, let us limit ourselves to the type of distortion which leads to the pear-shaped series of figures of equilibrium. For this, as we saw in the previous paper,  $u_1$  is of degree 3 in  $\xi$ ,  $\eta$ ,  $\zeta$ , so that  $w_1$  must by equation (24) be of degree unity, and from equation (25)  $w'_1$  must vanish. Similarly  $u_2$  is of degree 4, so that  $w_2$  is of degree 2,  $w'_2$  is of degree zero, and  $w''_2 = 0$ . Again  $u_3$  will be of degree 5,  $w_3$  of degree 3,  $w'_3$  of degree unity,  $w''_3 = 0$ ; and so on.

The set of equations for  $w_3$ ,  $w'_3$  ... now reduces to

7. Let us now introduce the operator D, already used in the previous paper (§ 14), defined by

$$D = \mathbf{A} \frac{\partial^2}{\partial \xi^2} + \mathbf{B} \frac{\partial^2}{\partial \tilde{\eta}^2} + \mathbf{C} \frac{\partial^2}{\partial \tilde{\zeta}^2} \quad . \quad . \quad . \quad . \quad . \quad (30)$$

By differentiation with respect to  $\lambda$ , we have

$$\frac{\partial D}{\partial \lambda} = \frac{1}{A^2} \frac{\partial^2}{\partial \xi^2} + \frac{1}{B^2} \frac{\partial^2}{\partial \eta^2} + \frac{1}{C^2} \frac{\partial^2}{\partial \xi^2}$$

so that  $\partial D/\partial \lambda$  is the same as  $\nabla^2$  transformed into  $\xi$ ,  $\eta$ ,  $\xi$  co-ordinates. We can now solve equations (24) to (29) at once by transforming into  $\xi$ ,  $\eta$ ,  $\xi$  co-ordinates.

Equation (24) becomes in  $\xi$ ,  $\eta$ ,  $\zeta$  co-ordinates

$$4 \frac{\partial w_1}{\partial \lambda} = -\frac{\partial \mathbf{D}}{\partial \lambda} u_1 = -\frac{\partial \mathbf{D}}{\partial \lambda} \mathbf{P},$$

and since P is a function of  $\hat{\xi}$ ,  $\eta$ ,  $\xi$  only, this has the integral

$$w_1 = -\frac{1}{4} DP.$$
 . . . . . . . . . . (31)

No constant of integration must be added, for D vanishes when  $\lambda = 0$  and  $w_1$  must also be made to vanish when  $\lambda = 0$  (cf. equations (23)). Thus equation (31) gives the true value of  $w_1$  and we have also seen above that  $w'_1 = w''_2 = \dots = 0$ .

The value of  $v_1$  is accordingly

$$v_1 = w_1 = -\frac{1}{4}DP = -\frac{1}{4}(\mathbf{A}P_{\xi\xi} + \mathbf{B}P_{\eta\eta} + \mathbf{C}P_{\zeta\zeta})$$
 . . . (32)

From §§ 6 and 4, we now have as the value of  $u_2$ ,

$$u_{2} = g_{2} + v_{1} g_{1}$$

$$= -\frac{1}{4} \left( \mathbf{A} \mathbf{P}_{\xi}^{2} + \mathbf{B} \mathbf{P}_{\eta}^{2} + \mathbf{C} \mathbf{P}_{\zeta}^{2} \right) + \mathbf{Q} - \frac{1}{4} \mathbf{P} \left( \mathbf{A} \mathbf{P}_{\xi \xi} + \mathbf{B} \mathbf{P}_{\eta \eta} + \mathbf{C} \mathbf{P}_{\zeta \zeta} \right)$$

$$= -\frac{1}{8} \mathbf{D} \mathbf{P}^{2} + \mathbf{Q}. \qquad (33)$$

The value of  $w_2$  can next be found from equation (26). The right-hand member reduces to  $-\nabla^2 u_2$ , and the equation, expressed in  $\xi$ ,  $\eta$ ,  $\zeta$  co-ordinates, becomes

$$4\frac{\partial w_2}{\partial \lambda} = -\frac{\partial \mathbf{D}}{\partial \lambda}u_2$$
$$= \frac{1}{8}\frac{\partial \mathbf{D}}{\partial \lambda}\mathbf{D}\mathbf{P}^2 - \frac{\partial \mathbf{D}}{\partial \lambda}\mathbf{Q},$$

of which the solution is

$$w_2 = \frac{1}{64} D^2 P^2 - \frac{1}{4} DQ$$
 . . . . . . . . . . . (34)

and similarly equation (27) leads to

$$w'_{2} = -\frac{1}{1536} D^{3}P^{2} + \frac{1}{64} D^{2}Q.$$
 (35)

These values for  $w_2$  and  $w'_2$  are identical with those obtained in the earlier paper, although obtained by a slightly different method. We now proceed to the third order terms.

On substituting for  $u_3$  its value as obtained in § 6, we find, in place of equation (28),

$$-4\left(\Sigmarac{x}{\mathrm{A}}rac{\partial w_{3}}{\partial x}+rac{\partial w_{3}}{\partial \lambda}
ight)=\left.
abla^{2}\left(g_{3}\!+v_{1}\!g_{2}
ight)+
abla^{2}\left(v_{2}\!g_{1}
ight)+4\Delta\left.rac{\partial}{\partial \lambda}\left(rac{g_{1}w'_{2}}{\Delta}
ight)
ight.$$

which, after a good deal of simplification,

$$= \nabla^{2} (g_{3} + v_{1}g_{2}) + \nabla^{2} (w_{2}P) + fw'_{2}\nabla^{2}P + 4P \frac{\partial w'_{2}}{\partial \lambda}$$

$$= \nabla^{2} (g_{3} + v_{1}g_{2}) + 2\sum_{\epsilon} \frac{1}{A^{2}} P_{\epsilon} \frac{\partial w_{2}}{\partial \xi} + (w_{2} + fw'_{2}) \nabla^{2}P - 4P \frac{\partial w'_{2}}{\partial \lambda}. \qquad (36)$$

Introducing the various values which have been obtained for  $g_3$ ,  $g_2$ ,  $v_1$ ,  $w_2$  and  $w'_2$ , we find, after simplification, that

$$\nabla^{2} (g_{3} + v_{1}g_{2}) + 2\Sigma \frac{1}{\mathbf{A}^{2}} \mathbf{P}_{\xi} \frac{\partial w_{2}}{\partial \xi} + w_{2}\nabla^{2}\mathbf{P}$$

$$= p\mathbf{A}^{2} \frac{\partial \mathbf{A}}{\partial \lambda} + q\mathbf{A}^{2} \frac{\partial \mathbf{B}}{\partial \lambda} + r\mathbf{A}\mathbf{B} \frac{\partial \mathbf{A}}{\partial \lambda} + s\mathbf{A}\mathbf{B} \frac{\partial \mathbf{C}}{\partial \lambda} + \dots$$

$$+ \boldsymbol{\varpi}\mathbf{A} \frac{\partial \mathbf{A}}{\partial \lambda} + \rho\mathbf{A} \frac{\partial \mathbf{B}}{\partial \lambda} + \sigma\mathbf{A} \frac{\partial \mathbf{C}}{\partial \lambda} + \dots + \alpha \frac{\partial \mathbf{A}}{\partial \lambda} + \dots$$
(37)

where

$$p = \frac{1}{32} \left[ \frac{\partial^{6}}{\partial \xi^{6}} \left( \frac{1}{6} P^{3} \right) - P \frac{\partial^{6}}{\partial \xi^{6}} \left( \frac{1}{2} P^{2} \right) \right],$$

$$q = \frac{1}{2}r = \frac{1}{32} \left[ \frac{\partial^{6}}{\partial \xi^{4} \partial \eta^{2}} \left( \frac{1}{6} P^{3} \right) - P \frac{\partial^{2}}{\partial \xi^{4} \partial \eta^{2}} \left( \frac{1}{2} P^{2} \right) \right],$$

$$s = \frac{1}{16} \left[ \frac{\partial^{6}}{\partial \xi^{2} \partial \eta^{2} \partial \xi^{2}} \left( \frac{1}{6} P^{3} \right) - P \frac{\partial^{6}}{\partial \xi^{2} \partial \eta^{2} \partial \xi^{2}} \left( \frac{1}{2} P^{2} \right) \right], \&c.,$$

$$\rho = -\frac{1}{4} \left[ \frac{\partial^{4}}{\partial \xi^{2} \partial \eta^{2}} \left( PQ \right) - P \frac{\partial^{4}}{\partial \xi^{2} \partial \eta^{2}} Q \right], \&c.,$$

$$\alpha = R_{\xi\xi}, \&c.$$

Relation (37) can accordingly be put in the form

$$\nabla^{2} (g_{3} + v_{1}g_{2}) + 2\Sigma \frac{1}{\mathbf{A}^{2}} \mathbf{P}_{\xi} \frac{\partial w_{2}}{\partial \xi} + w_{2}\nabla^{2}\mathbf{P} = \frac{\partial}{\partial \lambda} \left[ \frac{1}{96} \mathbf{D}^{3} \left( \frac{1}{6} \mathbf{P}^{3} \right) - \frac{1}{8} \mathbf{D}^{2} \left( \mathbf{PQ} \right) + \mathbf{DR} + 8\mathbf{P}w'_{2} \right].$$

Equation (36), after transformation to  $\xi$ ,  $\eta$ ,  $\zeta$  co-ordinates and integration with respect to  $\lambda$ , gives

$$w_3 = -\frac{1}{4} \left[ \frac{1}{96} D^3 \left( \frac{1}{6} P^3 \right) - \frac{1}{8} D^2 \left( PQ \right) + DR \right] - w'_2 P - \frac{1}{4} \int_0^{\lambda'} f w'_2 \nabla^2 P \, d\lambda. \quad (38)$$

Let us now put

so that  $\Lambda$  will be a function of  $\lambda$  only. We then have

$$\int_{0}^{\lambda'} f w'_{2} \nabla^{2} \mathbf{P} \, d\lambda = \int_{0}^{\lambda'} f \xi \frac{\partial \Lambda}{\partial \lambda} \, d\lambda = f \xi \Lambda - \xi \left( \xi^{2} + \eta^{2} + \xi^{2} \right) \int_{0}^{\lambda'} \Lambda \, d\lambda, \quad . \quad . \quad (40)$$

whence, on operating with  $\nabla^2$ ,

$$\nabla^2 \int_0^{\lambda'} f i v'_2 \nabla^2 \mathbf{P} \, d\lambda = \xi \frac{\partial}{\partial \lambda} \left\{ \left( \frac{6}{\mathbf{A}} + \frac{2}{\mathbf{B}} + \frac{2}{\mathbf{C}} \right) \int_0^{\lambda'} \Lambda \, d\lambda \right\}. \tag{41}$$

Equation (29), transformed to  $\hat{\xi}$ ,  $\eta$ ,  $\xi$  co-ordinates, now becomes

$$\begin{split} \frac{\partial w_3'}{\partial \lambda} &= -\frac{1}{8} \nabla^2 w_3 \\ &= \frac{1}{32} \left[ \frac{1}{96} \frac{\partial \mathbf{D}}{\partial \lambda} \, \mathbf{D}^3 \left( \frac{1}{6} \mathbf{P}^3 \right) \, - \frac{1}{8} \frac{\partial \mathbf{D}}{\partial \lambda} \, \mathbf{D}^2 \left( \mathbf{PQ} \right) + \frac{\partial \mathbf{D}}{\partial \lambda} \, \mathbf{D} \mathbf{R} \, \right] \\ &+ \frac{1}{8} \frac{\partial}{\partial \lambda} \left( \xi \Lambda \right) + \frac{1}{32} \xi \frac{\partial}{\partial \lambda} \left\{ \left( \frac{6}{\mathbf{A}} + \frac{2}{\mathbf{B}} + \frac{2}{\mathbf{C}} \right) \right\}_0^{\lambda'} \Lambda \, d\lambda \, \right\}, \end{split}$$

giving on integration,

$$w'_{3} = \frac{1}{32} \left[ \frac{1}{384} D^{4} \left( \frac{1}{6} P^{3} \right) - \frac{1}{24} D^{3} (PQ) + \frac{1}{2} D^{2} R \right] + \frac{1}{8} \xi \Lambda + \frac{1}{32} \xi \left( \frac{6}{A} + \frac{2}{B} + \frac{2}{C} \right) \int_{0}^{\lambda'} \Lambda d\lambda.$$

8. The solution is now complete as far as third order terms, but can be expressed in a more convenient form. We have found for the whole value of  $v_3$ ,

$$v_{3} = w_{3} + fw'_{3}$$

$$= -\frac{1}{4} \left[ \frac{1}{96} D^{3} \left( \frac{1}{6} P^{3} \right) - \frac{1}{8} D^{2} \left( PQ \right) + DR \right] - w'_{2} P$$

$$+ \frac{1}{32} f \left[ \frac{1}{384} D^{4} \left( \frac{1}{6} P^{3} \right) - \frac{1}{24} D^{3} \left( PQ \right) + \frac{1}{2} D^{2} R \right] + Z, \quad . \quad . \quad (42)$$

where Z is formed of terms involving the function  $\Lambda$ , and has its value given by

$$Z = \frac{1}{4}\xi \left(\xi^2 + \eta^2 + \xi^2\right) \int_0^{\lambda'} \Lambda \, d\lambda - \frac{1}{8}f \, \xi \, \Lambda$$
$$+ \frac{1}{8}f \, \xi \left(\frac{3}{2A} + \frac{1}{2B} + \frac{1}{2C}\right) \int_0^{\lambda'} \Lambda \, d\lambda.$$

The term Z in  $v_3$  gives rise to a term  $e^3fZ$  in  $\phi$ , and this in turn leads to a term

$$\psi(\lambda) e^{3} f Z = -\frac{\pi \rho abc}{\Delta} e^{3} f Z,$$

in the function  $\Phi$  (see §§ 4, 11 of the previous paper), from which the whole solution is derived. Using the value for Z which has just been obtained, we readily find that, in x, y, z co-ordinates,

$$-\frac{\pi\rho abc}{\Delta}e^{3}fZ = -\frac{1}{8}\pi\rho abc e^{3}\frac{\partial}{\partial\lambda'}\left\{\frac{f^{2}x}{\Delta A}\int_{0}^{\lambda'}\Lambda d\lambda\right\}. \qquad (43)$$

We found, however (see footnote to p. 32 of previous paper), that for a given potential problem, the value of  $\Phi$  is not unique. If any function  $\Phi$  gives a solution of the potential problem, then it was found that any other function of the form

$$\Phi + \frac{\partial}{\partial \lambda'} \left\{ F \int_0^{\lambda'} u \, d\lambda \right\}, \quad \dots \qquad (44)$$

will give a solution of the same problem, provided that F is any function of x, y, z, and  $\lambda$ , which vanishes when  $\lambda = \lambda'$  (i.e., when x, y, z, and  $\lambda$  are connected by relation (2)), and u is any function of  $\lambda$  whatever. Consistently with these conditions we may take

$$u = \Lambda$$
,  $F = \frac{1}{8}\pi\rho abc e^3 \frac{f(f+\phi)x}{\Delta A}$ ,

and the new solution (44) becomes

$$\Phi + \frac{1}{8}\pi\rho abc e^{3} \frac{\partial}{\partial \lambda'} \left\{ \frac{f(f+\phi) x}{\Delta A} \int_{0}^{\lambda'} \Lambda d\lambda \right\}. \qquad (45)$$

In this solution,  $\Phi$  already contains a term involving  $\Lambda$ , namely that given by expression (43). Combining this with the remaining term in expression (45), we find that the new solution can be put in the form

$$\Phi_0 + \frac{1}{8}\pi\rho \, abc \, e^3 \, \frac{\partial}{\partial \lambda'} \left\{ \frac{f\phi x}{\Delta A} \int_0^{\lambda'} \Lambda \, d\lambda \right\}, \quad . \quad . \quad . \quad . \quad (46)$$

where  $\Phi_0$  is the old solution  $\Phi$  with the terms in  $\Lambda$  omitted. The last term in expression (45), being proportional to  $e^3\phi$ , is of the fourth-order of small quantities. Thus in a solution as far as  $e^3$  only, this term may be omitted, and  $\Phi = \Phi_0$  will be a solution. In other words the term Z may be omitted entirely from equation (42), and the remaining terms will still give an accurate solution for  $v_3$ .

Omitting this Z-term, we obtain for the third order terms,

$$u_{3} + fv_{3} = u_{3} + f(w_{3} + fw'_{3})$$

$$= \frac{1}{32}D^{2}(\frac{1}{6}P^{3}) - \frac{1}{4}D(PQ) + R$$

$$- \frac{1}{4}f\{\frac{1}{96}D^{3}(\frac{1}{6}P^{3}) - \frac{1}{8}D^{2}(PQ) + DR\}$$

$$+ \frac{1}{32}f^{2}\{\frac{1}{384}D^{4}(\frac{1}{6}P^{3}) - \frac{1}{24}D^{3}(PQ) + \frac{1}{2}D^{2}R\}. \qquad (47)$$

This completes the solution of the general potential problem.

### Potential of the Pear-shaped Figure.

9. Collecting the results obtained in §§ 3–8, we have found that as far as terms of the third order of small quantities, a value of  $\phi$  which satisfies the necessary differential equation (6) is

$$\phi = e (u_{1} + fv_{1}) + e^{2} (u_{2} + fv_{2}) + e^{3} (u_{3} + fv_{3})$$

$$= e \left[ P - \frac{1}{4} f DP \right]$$

$$+ e^{2} \left[ Q - \frac{1}{8} DP^{2} + f \left\{ \frac{1}{64} D^{2} (P^{2}) - \frac{1}{4} DQ \right\} + f^{2} \left\{ -\frac{1}{1536} D^{3} P^{2} + \frac{1}{64} D^{2} Q \right\} \right]$$

$$+ e^{3} \left[ R - \frac{1}{4} f DPQ + \frac{1}{192} D^{2} P^{3} - \frac{1}{4} f \left\{ \frac{1}{576} D^{3} P^{3} - \frac{1}{8} D^{2} PQ + DR \right\} \right]$$

$$+ \frac{1}{32} f^{2} \left\{ \frac{1}{2304} D^{4} P^{3} - \frac{1}{24} D^{3} PQ + \frac{1}{2} D^{2} R \right\} \right]. \qquad (48)$$

At the boundary  $\lambda = 0$ , this value of  $\phi$  reduces to

$$\phi = eP + e^2Q + e^3R$$
, . . . . . . . . . (49)

and since P, Q, R are entirely at our disposal, this is capable of representing the most general displacement possible, as far as the third order of small quantities. We have, however, to save the printing of additional terms, already assumed that P is of a degree not higher than the third in x, y, z and Q of a degree not higher than the fourth. Subject to these limitations, the potential of the ellipsoid deformed in any way can be obtained by inserting the value (48) for  $\phi$  into equations (3) and (4).

10. We shall now limit ourselves to the distortion which was found, in the earlier paper, to lead to the pear-shaped figure of equilibrium. For this particular distortion we found (cf. equations (93) and (94) of the earlier paper),

$$Q = \frac{1}{4} \left[ L \xi^4 + M \eta^4 + N \zeta^4 + 2 l \eta^2 \zeta^2 + 2 m \zeta^2 \xi^2 + 2 n \xi^2 \eta^2 + 2 \left( p \xi^2 + q \eta^2 + r \zeta^2 \right) + s \right].$$
 (51)

We shall now assume for R the value

$$R = \frac{1}{4} \mathcal{E} \left[ \mathcal{L} \hat{\mathcal{E}}^4 + \mathcal{M} \eta^4 + \mathcal{N} \hat{\zeta}^4 + 2 \mathcal{I} \eta^2 \hat{\zeta}^2 + 2 \mathfrak{m} \hat{\zeta}^2 \hat{\mathcal{E}}^2 + 2 \mathfrak{m} \hat{\mathcal{E}}^2 \eta^2 + 2 \left( \mathfrak{p} \hat{\mathcal{E}}^2 + \mathfrak{q} \eta^2 + \mathfrak{r} \hat{\zeta}^2 \right) + \mathbf{5} \right], \tag{52}$$

this being found adequate to satisfy all the conditions for a figure of equilibrium of a rotating liquid mass.

11. The values of  $u_1+fv_1$  and of  $u_2+fv_2$  were calculated in the former paper (see equations (121), (122) and (132)). In the same way the value of  $u_3+fv_3$  as given by equation (47) is found to be

```
u_3 + fv_3 = \dot{\varepsilon}^5 \left[15\frac{3}{4}\mathbf{A}^2\alpha^3 + 2\frac{5}{8}\mathbf{A}\mathbf{B}\alpha^2\beta + 2\frac{5}{8}\mathbf{A}\mathbf{C}\alpha^2\gamma + \frac{3}{8}\mathbf{B}^2\alpha\beta^2 + \frac{1}{4}\mathbf{B}\mathbf{C}\alpha\beta\gamma + \frac{3}{8}\mathbf{C}^2\alpha\gamma^2\right]
                                  + \dot{\varepsilon}^3 \eta^2 \left[ 13\frac{1}{8}A^2\alpha^2\beta + 7\frac{1}{9}AB\alpha^2\beta + 2\frac{1}{9}AC\alpha\beta\gamma + 1\frac{7}{8}B^2\beta^3 + \frac{3}{4}BC\beta^2\gamma + \frac{3}{8}C^2\beta\gamma^2 \right]
                                   +\mathcal{E}^{3}\zeta^{2}\left[13\frac{1}{8}\mathbf{A}^{2}\alpha^{2}\gamma+2\frac{1}{2}\mathbf{A}\mathbf{B}\alpha\beta\gamma+7\frac{1}{2}\mathbf{A}\mathbf{C}\alpha\gamma^{2}+\frac{3}{8}\mathbf{B}^{2}\beta^{2}\gamma+\frac{3}{4}\mathbf{B}\mathbf{C}\beta\gamma^{2}+1\frac{7}{8}\mathbf{C}^{2}\gamma^{3}\right]
                                  +\dot{\varepsilon}\eta^4 \left[1\frac{7}{8}\mathbf{A}^2\alpha\beta^2+1\frac{7}{8}\mathbf{A}\mathbf{B}\beta^3+\frac{3}{8}\mathbf{A}\mathbf{C}\beta^2\gamma\right]
                                  +\dot{\varepsilon}\dot{\zeta}^4 \left[1\frac{7}{8}\mathbf{A}^2\alpha\gamma^2 + \frac{3}{8}\mathbf{A}\mathbf{B}\beta\gamma^2 + 1\frac{7}{8}\mathbf{A}\mathbf{C}\gamma^3\right]
                                  +\hat{\xi}\eta^2\xi^2\left[3\frac{3}{4}\mathbf{A}^2\alpha\beta\gamma+2\frac{1}{4}\mathbf{A}\mathbf{B}\beta^2\gamma+2\frac{1}{4}\mathbf{A}\mathbf{C}\beta\gamma^2\right]
                                  +\dot{\xi}^{3}\kappa \left[13\frac{1}{8}\mathbf{A}^{2}\alpha^{2}\right] +2\frac{1}{2}\mathbf{A}\mathbf{B}\alpha\beta +2\frac{1}{2}\mathbf{A}\mathbf{C}\alpha\gamma +\frac{3}{8}\mathbf{B}^{2}\beta^{2} +\frac{1}{4}\mathbf{B}\mathbf{C}\beta\gamma +\frac{3}{8}\mathbf{C}^{2}\gamma^{2}\right]
                                  +\hat{\varepsilon}_{\eta}^{2}\kappa \left[ 3\frac{3}{4}\mathbf{A}^{2}\alpha\beta + 2\frac{1}{4}\mathbf{A}\mathbf{B}\beta^{2} + \frac{3}{4}\mathbf{A}\mathbf{C}\beta\gamma \right]
                                  +\dot{\varepsilon}\zeta^2\kappa \[ 3\frac{3}{4}\mathbf{A}^2\alpha\gamma + \frac{3}{4}\mathbf{A}\mathbf{B}\beta\gamma + 2\frac{1}{4}\mathbf{A}\mathbf{C}\gamma^2 \]
                                  +\hat{\xi}\kappa^2 \left[\begin{array}{ccc} 1\frac{7}{8}\mathbf{A}^2\alpha & + \frac{3}{8}\mathbf{A}\mathbf{B}\beta & + \frac{3}{8}\mathbf{A}\mathbf{C}\gamma\end{array}\right]
                                                                                             +\frac{1}{8}\mathbf{B}\left(\mathbf{L}\boldsymbol{\beta}+2n\boldsymbol{\alpha}\right) +\frac{1}{8}\mathbf{C}\left(\mathbf{L}\boldsymbol{\gamma}+2m\boldsymbol{\alpha}\right)
                                 -\xi^5 \left[\begin{array}{cc} 2\frac{5}{8}\mathbf{A}\mathbf{L}\alpha\end{array}\right]
                                 -\hat{\xi}^{3}\eta^{2}\left[1\frac{1}{4}\mathbf{A}\left(\mathbf{L}\beta+2n\alpha\right)+\frac{3}{4}\mathbf{B}\left(\mathbf{M}\alpha+2n\beta\right)+\frac{1}{4}\mathbf{C}\left(l\alpha+m\beta+n\gamma\right)\right]
                                 -\xi^3\xi^2 [ 1\frac{1}{4}\mathbf{A}\left(\mathbf{L}\gamma+2m\alpha\right) + \frac{1}{4}\mathbf{B}\left(l\alpha+m\beta+n\gamma\right) + \frac{3}{4}\mathbf{C}\left(\mathbf{N}\alpha+2n\gamma\right)]
                                 -\xi \eta^4 \left[ \frac{3}{8} \mathbf{A} \left( \mathbf{M} \alpha + 2n\beta \right) + \frac{17}{8} \mathbf{B} \mathbf{M} \beta \right] + \frac{1}{8} \mathbf{C} \left( \mathbf{M} \gamma + 2l\beta \right) \right]
                                 -\xi \xi^4 \left[ \frac{3}{8} \mathbf{A} \left( \mathbf{N} \alpha + 2n \gamma \right) + \frac{1}{8} \mathbf{B} \left( \mathbf{N} \beta + 2l \gamma \right) + 1 \frac{7}{8} \mathbf{C} \mathbf{N} \gamma \right]
                                 -\xi\eta^2\xi^2\left[\frac{3}{4}\mathbf{A}\left(l\alpha+m\beta+n\gamma\right)+\frac{3}{4}\mathbf{B}\left(\mathbf{M}\gamma+2l\beta\right)\right]+\frac{3}{4}\mathbf{C}\left(\mathbf{N}\beta+2l\gamma\right)\right]
                                 -\xi^{3} \left[ 1\frac{1}{4}\mathbf{A} \left( \mathbf{L}\kappa + 2\alpha p \right) + \frac{1}{4}\mathbf{B} \left( n\kappa + \alpha q + \beta p \right) + \frac{1}{4}\mathbf{C} \left( m\kappa + \gamma p + \alpha r \right) \right]
                                 -\xi \eta^{2} \left[ \frac{3}{4} \mathbf{A} \left( n\kappa + \alpha q + \beta p \right) + \frac{3}{4} \mathbf{B} \left( \mathbf{M} \kappa + 2\beta q \right) + \frac{1}{4} \mathbf{C} \left( l\kappa + \gamma q + \beta r \right) \right]
                                 -\xi \xi^2 \left[ \frac{3}{4} \mathbf{A} \left( m\kappa + \gamma p + \alpha r \right) + \frac{1}{4} \mathbf{B} \left( l\kappa + \gamma q + \beta r \right) + \frac{3}{4} \mathbf{C} \left( N\kappa + 2\gamma r \right) \right]
                                 -\xi \begin{bmatrix} \frac{3}{8}\mathbf{A}(2p\kappa+s\alpha) + \frac{1}{8}\mathbf{B}(2a\kappa+s\beta) + \frac{1}{8}\mathbf{C}(2r\kappa+s\gamma) \end{bmatrix}
                                +\frac{1}{4}\xi \left[ 2\xi^{4} + \Omega \eta^{4} + N \xi^{4} + 2 \ln^{2} \xi^{2} + 2 m \xi^{2} \xi^{2} + 2 n \xi^{2} \eta^{2} + 2 (p \xi^{2} + q \eta^{2} + r \xi^{2}) + 5 \right]
```

$$-\xi^{3}f\left[26\frac{1}{4}\text{A}^{3}a^{3} + \frac{1}{16}\text{B}^{3}\beta^{3} + \frac{1}{16}\text{C}^{3}\gamma^{3} + 6\frac{9}{16}\text{A}^{2}\text{Ba}^{2}\beta + 6\frac{9}{16}\text{A}^{2}\text{Ca}^{2}\gamma \right. \\ + 1\frac{7}{8}\text{AB}^{2}\alpha\beta^{2} + 1\frac{7}{8}\text{AC}^{2}\alpha\gamma^{2} + 1\frac{1}{4}\text{ABC}\alpha\beta\gamma + \frac{3}{16}\text{BC}^{2}\beta\gamma^{2} \right] \\ -\xi^{3}f\left[6\frac{9}{16}\text{A}^{3}\alpha^{2}\beta + 5\frac{5}{8}\text{A}^{2}\text{B}\alpha\beta^{2} + 1\frac{7}{8}\text{A}^{2}\text{C}\alpha\beta\gamma + 2\frac{1}{16}\text{AB}^{2}\beta^{3} + \frac{9}{16}\text{AC}^{2}\beta\gamma^{2} + 1\frac{1}{8}\text{ABC}\beta^{2}\gamma \right] \\ -\xi\xi^{2}f\left[6\frac{9}{16}\text{A}^{3}\alpha^{2}\gamma + 1\frac{7}{8}\text{A}^{2}\text{B}\alpha\beta\gamma + 5\frac{5}{8}\text{A}^{2}\text{C}\alpha\gamma^{2} + \frac{9}{16}\text{AB}^{2}\beta^{2}\gamma + 2\frac{1}{16}\text{AC}^{2}\gamma^{3} + 1\frac{1}{8}\text{ABC}\beta\gamma^{2}\right] \\ -\xi\xi^{2}f\left[6\frac{9}{16}\text{A}^{3}\alpha^{2}\gamma + 1\frac{7}{8}\text{A}^{2}\text{B}\alpha\beta\gamma + 5\frac{5}{8}\text{A}^{2}\text{C}\alpha\gamma^{2} + \frac{9}{16}\text{AB}^{2}\beta^{2}\gamma + 2\frac{1}{16}\text{AC}^{2}\gamma^{3} + 1\frac{1}{8}\text{ABC}\beta\gamma^{2}\right] \\ -\xi^{3}f\left[6\frac{9}{16}\text{A}^{3}\alpha^{2}\kappa + 1\frac{7}{8}\text{A}^{2}\text{B}\alpha\beta\kappa + 1\frac{7}{8}\text{A}^{2}\text{C}\alpha\gamma\kappa + \frac{9}{16}\text{AB}^{2}\beta^{2}\kappa + \frac{9}{16}\text{AC}^{2}\gamma^{2}\kappa + \frac{3}{8}\text{ABC}\beta\gamma\kappa \right] \\ +\xi^{3}f\left[6\frac{9}{16}\text{A}^{2}\text{L}\alpha + \frac{3}{16}\text{B}^{2}\left(\text{M}\alpha + 2n\beta\right) + \frac{3}{16}\text{C}^{2}\left(\text{N}\alpha + 2n\gamma\right) + \frac{5}{8}\text{AB}\left(\text{L}\beta + 2n\alpha\right) \\ +\frac{5}{8}\text{AC}\left(\text{L}\gamma + 2m\alpha\right) + \frac{1}{8}\text{BC}\left(\text{L}\alpha + m\beta + n\gamma\right)\right] \\ +\xi^{3}f\left[\frac{1}{16}\text{A}^{2}\left(\text{L}\beta + 2n\alpha\right) + 2\frac{1}{16}\text{B}^{2}\text{M}\beta + \frac{3}{16}\text{C}^{2}\left(\text{N}\beta + 2l\gamma\right) + 1\frac{1}{8}\text{AB}\left(\text{M}\alpha + 2n\beta\right) \\ +\frac{3}{8}\text{AC}\left(l\alpha + m\beta + n\gamma\right) + \frac{3}{8}\text{BC}\left(\text{M}\gamma + 2l\beta\right)\right] \\ +\xi^{2}f\left[\frac{1}{16}\text{A}^{2}\left(\text{L}\gamma + 2m\alpha\right) + \frac{3}{16}\text{B}^{2}\left(\text{M}\gamma + 2l\beta\right) + 2\frac{1}{16}\text{C}^{2}\text{N}\gamma + \frac{3}{8}\text{AB}\left(l\alpha + m\beta + n\gamma\right) \\ + 1\frac{1}{8}\text{AC}\left(\text{N}\alpha + 2n\gamma\right) + \frac{3}{8}\text{BC}\left(\text{N}\beta + 2l\gamma\right)\right] \\ +\xi^{3}f\left[\frac{1}{16}\text{A}^{2}\left(\text{L}\kappa + 2\alpha p\right) + \frac{3}{16}\text{B}^{2}\left(\text{M}\kappa + 2\beta q\right) + \frac{3}{16}\text{C}^{2}\left(\text{N}\kappa + 2\gamma r\right) + \frac{3}{8}\text{AB}\left(n\kappa + \alpha q + \beta p\right) \\ +\frac{3}{8}\text{AC}\left(m\kappa + \gamma p + \alpha r\right) + \frac{1}{8}\text{BC}\left(l\kappa + \gamma q + \beta r\right)\right] \\ -\xi^{3}f\left[\frac{1}{4}\text{M}A + \frac{1}{4}\text{M}B + \frac{1}{4}\text{MC}\right] \\ -\xi^{2}f\left[\frac{3}{4}\text{M}A + \frac{1}{4}\text{M}B + \frac{1}{4}\text{M}C\right] \\ +\xi^{2}f\left[\frac{3}{4}\text{M}A + \frac{1}{4}\text{M}A + \frac{$$

where f stands for  $A\hat{\xi}^2 + B\eta^2 + C\xi^2 - 1$ , and G is given by

$$G = A \left\{ \frac{315}{64} A^{3} \alpha^{3} + \frac{105}{64} A^{2} B \alpha^{2} \beta + \frac{105}{64} A^{2} C \alpha^{2} \gamma + \frac{45}{64} A B^{2} \alpha \beta^{2} \right. \\ + \frac{45}{64} A C^{2} \alpha \gamma^{2} + \frac{15}{32} A B C \alpha \beta \gamma + \frac{15}{64} B^{3} \beta^{3} + \frac{15}{64} C^{3} \gamma^{3} \\ + \frac{9}{64} B^{2} C \beta^{2} \gamma + \frac{9}{64} B C^{2} \beta \gamma^{2} \right\} \\ - \frac{105}{64} A^{3} L \alpha - \frac{15}{64} A^{2} B \left( L \beta + 2n\alpha \right) - \frac{15}{64} A^{2} C \left( L \gamma + 2m\alpha \right) \\ - \frac{9}{64} A B^{2} \left( M \alpha + 2n\beta \right) - \frac{9}{64} A C^{2} \left( N \alpha + 2n\gamma \right) - \frac{3}{32} A B C \left( l\alpha + m\beta + n\gamma \right) \\ - \frac{15}{64} B^{3} M \beta - \frac{15}{64} C^{3} N \gamma - \frac{3}{64} B^{2} C \left( M \gamma + 2l\beta \right) - \frac{3}{64} B C^{2} \left( N \beta + 2l\gamma \right) \\ + \frac{15}{32} A^{2} L + \frac{3}{32} B^{2} \mathcal{H} + \frac{3}{32} C^{2} \mathcal{D} + \frac{1}{16} B C l + \frac{3}{16} A C m + \frac{3}{16} A B n. \qquad (54)$$

12. The potential of the distorted ellipsoid

$$f + eP + e^{2}Q + e^{3}R = 0$$
, . . . . . . . (55)

can now be written down as far as terms in  $e^3$ . The terms in e and  $e^2$ , which of course involve only P and Q, have been calculated in the previous paper. The terms in  $e^3$  in  $V_b$ , the potential at the boundary  $\lambda = 0$ , are (ef equation (3)),

$$e^{3} \int_{0}^{\infty} \psi(\lambda) \left( u_{3} + f v_{3} \right) d\lambda = -\pi \rho abc \, e^{3} \int_{0}^{\infty} \frac{u_{3} + f v_{3}}{\Delta} d\lambda, \quad . \quad . \quad . \quad (56)$$

in which  $u_3+fv_3$  has the value just given in equation (53).

Let us put

$$\int_{0}^{\infty} \frac{u_{3} + fv_{3}}{\Delta} d\lambda = x \left( \mathfrak{c}_{11} x^{4} + \mathfrak{c}_{22} y^{4} + \mathfrak{c}_{33} z^{4} + \mathfrak{c}_{12} x^{2} y^{2} + \mathfrak{c}_{31} z^{2} x^{2} + \mathfrak{c}_{23} y^{2} z^{2} + \mathfrak{d}_{1} x^{2} + \mathfrak{d}_{2} y^{2} + \mathfrak{d}_{3} z^{2} + \mathfrak{d}_{4} \right). \tag{57}$$

The values of the various coefficients in this expression are found to be as follows:—

$$\begin{split} \mathfrak{c}_{11} &= \int_{0}^{\infty} \frac{1}{\Delta \Lambda^{3}} \left[ 15\frac{3}{4} \mathbf{A}^{2} a^{3} + 2\frac{5}{8} \mathbf{A} \mathbf{B} a^{2} \beta + 2\frac{5}{8} \mathbf{A} \mathbf{C} a^{2} \gamma + \frac{3}{8} \mathbf{B}^{2} a \beta^{2} + \frac{1}{4} \mathbf{B} \mathbf{C} a \beta \gamma \right. \\ &\quad + \frac{3}{8} \mathbf{C}^{2} a \gamma^{2} - 2\frac{5}{8} \mathbf{A} \mathbf{L} a - \frac{1}{8} \mathbf{B} \left( \mathbf{L} \beta + 2na \right) - \frac{1}{8} \mathbf{C} \left( \mathbf{L} \gamma + 2ma \right) + \frac{1}{4} \frac{1}{4} \right] d\lambda \\ &\quad - \int_{0}^{\infty} \frac{1}{\Delta \Lambda^{4}} \left[ 26\frac{1}{4} \mathbf{A}^{3} a^{3} + \frac{5}{16} \mathbf{B}^{3} \beta^{2} + \frac{5}{16} \mathbf{C}^{2} \gamma^{2} + 6\frac{5}{16} \mathbf{A}^{2} \mathbf{B} a^{2} \beta + 6\frac{5}{16} \mathbf{A}^{2} \mathbf{C} a^{2} \gamma \right. \\ &\quad + 1\frac{7}{8} \mathbf{A} \mathbf{B}^{2} a \beta^{2} + 1\frac{7}{8} \mathbf{A} \mathbf{C}^{2} a \gamma^{2} + 1\frac{1}{4} \mathbf{A} \mathbf{B} \mathbf{C} a \beta \gamma + \frac{3}{16} \mathbf{B}^{2} \mathbf{C} \beta^{2} \gamma + \frac{3}{16} \mathbf{B}^{2} \mathbf{C}^{2} \beta \gamma^{2} \right] d\lambda \\ &\quad + \int_{0}^{\infty} \frac{1}{\Delta \Lambda^{4}} \left[ 6\frac{3}{16} \mathbf{A}^{2} \mathbf{L} a + \frac{1}{3} c^{2} \mathbf{B} \mathbf{C} \left( \mathbf{M} a + 2n\beta \right) + \frac{3}{16} \mathbf{C}^{2} \left( \mathbf{N} a + 2n\gamma \right) \right. \\ &\quad + \frac{5}{8} \mathbf{A} \mathbf{B} \left( \mathbf{L} \beta + 2na \right) + \frac{5}{8} \mathbf{A} \mathbf{C} \left( \mathbf{L} \gamma + 2ma \right) + \frac{1}{8} \mathbf{B} \mathbf{C} \left( la + m\beta + n\gamma \right) \right] d\lambda \\ &\quad - \int_{0}^{\infty} \frac{1}{\Delta \Lambda^{3}} \left[ 1\frac{1}{4} \mathbf{A} \frac{3}{4} + \frac{1}{4} \mathbf{B} \mathbf{n} + \frac{1}{4} \mathbf{C} \mathbf{m} \right] + \int_{0}^{\infty} \frac{\mathbf{C}}{\Delta \mathbf{A}^{3}} d\lambda \right. \qquad (58) \\ &\mathbf{c}_{12} = \int_{0}^{\infty} \frac{1}{\Delta \Lambda^{3}} \mathbf{B}^{2} \left[ 13\frac{1}{8} \mathbf{A}^{2} a^{2} \beta + 7\frac{1}{2} \mathbf{A} \mathbf{B} a \beta^{2} + 2\frac{1}{2} \mathbf{A} \mathbf{C} a \beta \gamma + 1\frac{7}{8} \mathbf{B}^{2} \beta^{3} + \frac{3}{4} \mathbf{B} \mathbf{C} \beta^{2} \gamma \right. \\ &\quad + \frac{3}{8} \mathbf{C}^{2} \beta \gamma^{2} - 1\frac{1}{4} \mathbf{A} \left( \mathbf{L} \beta + 2na \right) - \frac{3}{4} \mathbf{B} \left( \mathbf{M} a + 2n\beta \right) - \frac{1}{4} \mathbf{C} \left( la + m\beta + n\gamma \right) + \frac{1}{2} \mathbf{n} \right] d\lambda \\ &\quad - \int_{0}^{\infty} \frac{1}{\Delta \Lambda^{3}} \mathbf{B} \left[ 26\frac{1}{4} \mathbf{A}^{3} a^{2} + 7\frac{5}{6} \mathbf{B}^{3} \beta^{3} + 1\frac{5}{6} \mathbf{C}^{3} \alpha \gamma^{2} + 6\frac{1}{16} \mathbf{A}^{2} \mathbf{B} a^{2} \beta + 6\frac{1}{16} \mathbf{A}^{2} \mathbf{C} a^{2} \gamma \right. \\ &\quad + 1\frac{7}{8} \mathbf{A} \mathbf{B}^{2} a \beta^{2} + 1\frac{7}{8} \mathbf{A} \mathbf{C}^{2} a \gamma^{2} + 1\frac{1}{4} \mathbf{A} \mathbf{B} \mathbf{C} a \beta \gamma + \frac{7}{16} \mathbf{B}^{2} \mathbf{C} \beta^{2} \gamma \right. \\ &\quad + 1\frac{7}{6} \mathbf{A}^{2} \mathbf{B}^{2} \left( \mathbf{L} \beta + 2na \right) + 2\frac{7}{16} \mathbf{B}^{2} \mathbf{B} \beta + \frac{7}{16} \mathbf{B}^{2} \mathbf{C} \left( \mathbf{B} \gamma + 2l\gamma \right) \\ &\quad + 1\frac{1}{8} \mathbf{A} \mathbf{B} \left( \mathbf{A} \mathbf{A} + 2n\beta \right) + \frac{3}{8} \mathbf{A} \mathbf{C} \left( la + m\beta + n\gamma \right) + \frac{3}{8} \mathbf{B} \mathbf{C} \left( \mathbf{M} \gamma + 2l\beta \right) \right] d\lambda \\ &\quad$$

The value of  $\mathfrak{c}_{13}$  can be written down from symmetry.

The value of  $\mathfrak{e}_{33}$  can be written down from symmetry.

The values of the four coefficients  $\mathfrak{d}_1$ ,  $\mathfrak{d}_2$ ,  $\mathfrak{d}_3$ ,  $\mathfrak{d}_4$  are most conveniently expressed in the form:—

$$\mathfrak{d}_{1} = \delta_{1} - \int_{0}^{\infty} \frac{1}{\Delta \mathbf{A}^{2}} \left( \frac{3}{4} \mathfrak{p} \mathbf{A} + \frac{1}{4} \mathfrak{q} \mathbf{B} + \frac{1}{4} \mathfrak{r} \mathbf{C} \right) d\lambda + \frac{1}{2} \mathfrak{p} \int_{0}^{\infty} \frac{d\lambda}{\Delta \mathbf{A}^{3}} - 2 \int_{0}^{\infty} \frac{\mathbf{G}}{\Delta \mathbf{A}^{2}} d\lambda, \quad . \quad (62)$$

$$\mathfrak{d}_{2} = \delta_{2} - \int_{0}^{\infty} \frac{1}{\Delta AB} \left( \frac{3}{4} \mathfrak{p} \mathbf{A} + \frac{1}{4} \mathfrak{q} \mathbf{B} + \frac{1}{4} \mathfrak{r} \mathbf{C} \right) d\lambda + \frac{1}{2} \mathfrak{q} \int_{0}^{\infty} \frac{d\lambda}{\Delta AB^{2}} - 2 \int_{0}^{\infty} \frac{G}{\Delta AB} d\lambda, \quad (63)$$

$$\mathfrak{d}_{3} = \delta_{3} - \int_{0}^{\infty} \frac{1}{\Delta AC} \left( \frac{3}{4} \mathfrak{p} \mathbf{A} + \frac{1}{4} \mathfrak{q} \mathbf{B} + \frac{1}{4} \mathfrak{r} \mathbf{C} \right) d\lambda + \frac{1}{2} \mathfrak{r} \int_{0}^{\infty} \frac{d\lambda}{\Delta AC^{2}} - 2 \int_{0}^{\infty} \frac{G}{\Delta AC} d\lambda, \quad . \quad (64)$$

$$\mathfrak{d}_{4} = \delta_{4} + \int_{0}^{\infty} \frac{1}{\Delta \mathbf{A}} \left( \frac{3}{4} \mathfrak{p} \mathbf{A} + \frac{1}{4} \mathfrak{q} \mathbf{B} + \frac{1}{4} \mathfrak{r} \mathbf{C} \right) d\lambda + \frac{1}{4} \mathfrak{s} \int_{0}^{\infty} \frac{d\lambda}{\Delta \mathbf{A}} - \int_{0}^{\infty} \frac{\mathbf{G}}{\Delta \mathbf{A}} d\lambda, \quad . \quad (65)$$

where  $\delta_1$ ,  $\delta_2$ ,  $\delta_3$ ,  $\delta_4$  are quantities which do not depend on  $\mathfrak{p}$ ,  $\mathfrak{q}$ ,  $\mathfrak{r}$ ,  $\mathfrak{s}$ , being given by the following equations:—

$$\begin{split} \delta_{1} &= \int_{0}^{\infty} \frac{1}{\Delta \mathbf{A}^{3}} \left[ \kappa \left( 13\frac{1}{8}\mathbf{A}^{2}\alpha^{2} + 2\frac{1}{2}\mathbf{A}\mathbf{B}\alpha\beta + 2\frac{1}{2}\mathbf{A}\mathbf{C}\alpha\gamma + \frac{2}{8}\mathbf{B}^{2}\beta^{2} + \frac{1}{4}\mathbf{B}\mathbf{C}\beta\gamma + \frac{2}{8}\mathbf{C}^{2}\gamma^{2} \right) \\ &- 1\frac{1}{4}\mathbf{A} \left( \mathbf{L}\kappa + 2\alpha p \right) - \frac{1}{4}\mathbf{B} \left( n\kappa + \alpha q + \beta p \right) - \frac{1}{4}\mathbf{C} \left( m\kappa + p\gamma + r\alpha \right) \\ &+ 26\frac{1}{4}\mathbf{A}^{2}\alpha^{3} + \frac{1}{5}\mathbf{B}^{2}\beta^{3} + \frac{1}{5}\mathbf{C}^{3}\gamma^{2} + 6\frac{1}{5}\mathbf{C}^{3}\mathbf{A}^{2}\mathbf{B}\alpha^{2}\beta + 6\frac{1}{15}\mathbf{A}^{2}\mathbf{C}\alpha\gamma \\ &+ 1\frac{2}{8}\mathbf{A}\mathbf{B}^{2}\alpha\beta^{2} + 1\frac{1}{8}\mathbf{A}\mathbf{C}^{2}\alpha\gamma^{2} + 1\frac{1}{4}\mathbf{A}\mathbf{B}\mathbf{C}\alpha\beta\gamma + \frac{1}{15}\mathbf{B}^{2}\mathbf{C}\beta^{2}\gamma + \frac{3}{15}\mathbf{B}\mathbf{C}^{2}\beta\gamma^{2} \right] d\lambda \\ &- \int_{0}^{\infty} \frac{\kappa}{\Delta \mathbf{A}^{2}} \left[ 6\frac{9}{16}\mathbf{A}^{3}\alpha^{2} + 1\frac{7}{8}\mathbf{A}^{2}\mathbf{B}\alpha\beta + 1\frac{7}{8}\mathbf{A}^{2}\mathbf{C}\alpha\gamma + \frac{9}{15}\mathbf{A}\mathbf{B}^{2}\beta^{2} + \frac{9}{16}\mathbf{A}\mathbf{C}^{2}\gamma^{2} + \frac{3}{8}\mathbf{A}\mathbf{B}\mathbf{C}\beta\gamma \right] d\lambda \\ &- \int_{0}^{\infty} \frac{1}{\Delta \mathbf{A}^{3}} \left[ 6\frac{9}{16}\mathbf{A}^{3}\alpha^{2} + 1\frac{7}{8}\mathbf{A}^{2}\mathbf{B}\alpha\beta + 1\frac{7}{8}\mathbf{A}^{2}\mathbf{C}\alpha\gamma + \frac{9}{16}\mathbf{B}^{2}\alpha^{2} + \frac{9}{16}\mathbf{A}\mathbf{C}^{2}\gamma^{2} + \frac{3}{8}\mathbf{A}\mathbf{B}\mathbf{C}\beta\gamma \right] d\lambda \\ &- \int_{0}^{\infty} \frac{1}{\Delta \mathbf{A}^{3}} \left[ 6\frac{9}{16}\mathbf{A}^{3}\alpha^{2} + 1\frac{3}{8}\mathbf{B}^{2}\left( \mathbf{M}\alpha + 2n\beta \right) + \frac{7}{16}\mathbf{C}^{2}\left( \mathbf{N}\alpha + 2m\gamma \right) \\ &+ \frac{7}{8}\mathbf{A}\mathbf{B} \left( \mathbf{L}\beta + 2n\alpha \right) + \frac{5}{8}\mathbf{A}\mathbf{C} \left( \mathbf{L}\gamma + 2m\alpha \right) + \frac{1}{8}\mathbf{B}\mathbf{C} \left( l\alpha + m\beta + n\gamma \right) \right] d\lambda \\ &+ \int_{0}^{\infty} \frac{1}{\Delta \mathbf{A}^{3}} \left[ 1\frac{1}{4}\mathbf{A}\mathbf{B} + \frac{1}{4}\mathbf{B}\mathbf{n} + \frac{1}{4}\mathbf{C}\mathbf{m} \right] d\lambda \\ &+ \int_{0}^{\infty} \frac{1}{\Delta \mathbf{A}^{3}} \left[ 1\frac{1}{4}\mathbf{A}\mathbf{B} + \frac{1}{4}\mathbf{B}\mathbf{n} + \frac{1}{4}\mathbf{C}\mathbf{m} \right] d\lambda \\ &+ \int_{0}^{\infty} \frac{1}{\Delta \mathbf{A}^{3}} \left[ n\kappa + \alpha q + \beta p \right) - \frac{3}{4}\mathbf{B} \left( m\kappa + 2\beta q \right) - \frac{1}{4}\mathbf{C} \left( l\kappa + \gamma q + \beta r \right) \\ &+ 6\frac{3}{6}\mathbf{A}\mathbf{B}^{2}\beta^{3} + \frac{9}{16}\mathbf{A}\mathbf{C}^{2}\beta\gamma^{2} + \frac{3}{8}\mathbf{A}\mathbf{C}\beta\gamma \right) \\ &- \frac{3}{4}\mathbf{A} \left( n\kappa + \alpha q + \beta p \right) - \frac{3}{4}\mathbf{B} \left( m\kappa + 2\beta q \right) - \frac{1}{4}\mathbf{C} \left( l\kappa + \gamma q + \beta r \right) \\ &+ 6\frac{3}{6}\mathbf{A}\mathbf{B}^{2}\beta^{3} + \frac{9}{16}\mathbf{A}\mathbf{C}^{2}\beta\gamma^{2} + \frac{3}{8}\mathbf{A}\mathbf{C}\beta\gamma \right) \\ &+ \frac{1}{6}\mathbf{A}\mathbf{B} \left[ 6\frac{9}{16}\mathbf{A}^{3}\alpha^{2} + 1\frac{7}{8}\mathbf{A}^{2}\mathbf{B}\alpha\beta + 1\frac{7}{8}\mathbf{A}^{2}\mathbf{C}\alpha\beta + \frac{9}{16}\mathbf{A}\mathbf{B}^{2}\beta^{2} + \frac{9}{16}\mathbf{A}\mathbf{C}^{2}\gamma^{2} + \frac{3}{8}\mathbf{A}\mathbf{B}\mathbf{C}\beta\gamma \right] d\lambda \\ &- \int_{0}^{\infty} \frac{\kappa}{\Delta\mathbf{A}\mathbf{B}} \left[ 6\frac{9}{16}\mathbf{A}^{3}\alpha^{2} + 1\frac{7}{8}\mathbf{A}^{2}\mathbf{B}\mathbf{$$

The value of  $\delta_3$  can be written down from symmetry; that of  $\delta_4$ , which is of the same general type, will not be required in the present investigation.

13. This completes the solution of the particular potential problem which we have had in hand. It might naturally be feared that some mistake might have been made either in principle or in detail, and it must be remembered that even one mistake might invalidate the answer to the whole problem. I have, therefore, both here and elsewhere, taken the utmost care to check the accuracy of my work in every way. The following will, I think, show that no error need be feared in the solution which has just been obtained.

The value of  $V_i$ , if obtained accurately, ought to satisfy  $\nabla^2 V_i = -4\pi\rho$ , and the term  $-4\pi\rho$  must come entirely from the terms independent of e in  $V_i$ . Thus the terms in  $V_i$  which are multiplied by e,  $e^2$  and  $e^3$  ought separately to be spherical harmonics.

It was verified in the previous paper that the terms in e and  $e^2$  were in actual fact of this form. The terms in  $e^3$  will be harmonic if the quantity on the right of equation (57) is harmonic, and the conditions for this are expressed by the equations

$$10\mathfrak{c}_{11} + \mathfrak{c}_{12} + \mathfrak{c}_{13} = 0, \dots$$
 (68)

$$6\mathfrak{c}_{22} + 3\mathfrak{c}_{12} + \mathfrak{c}_{23} = 0, \dots, (69)$$

$$6\mathfrak{c}_{33} + 3\mathfrak{c}_{13} + \mathfrak{c}_{23} = 0, \dots$$
 (70)

I have inserted the values just obtained for  $\mathfrak{c}_1, \mathfrak{c}_{12}, \ldots \mathfrak{d}_1, \ldots$  in these equations, and have verified that they are all satisfied. (The necessary transformations of the various integrals are tedious, but involve no special difficulties.)

It follows that the solution we have obtained gives accurately the potential of some solid of uniform density  $\rho$ . By the method explained in the earlier sections of the previous paper, it is easy to work the problem backwards and to verify that the equation of the boundary of the solid in question is obtained by putting  $\lambda = 0$  in the equation  $f + \phi = 0$ . Thus we verify that our solution gives accurately the potential of the solid of boundary

$$f + eP + e^2Q + e^3R = 0.$$
 (72)

Conditions that Pear-shaped Figure shall be one of Equilibrium for a Rotating Liquid.

14. In order that the figure determined by equation (72) shall be one of equilibrium for a rotating liquid, the potential at the boundary plus  $\frac{1}{2}w^2(x^2+y^2)$  must, as in equation (98) of the former paper, be identical with

$$-\pi\rho abc\theta \left\{f+e\mathbf{P}+e^2\mathbf{Q}+e^3\mathbf{R}\right\}+$$
a constant.

Let us limit ourselves to the terms in  $e^3$ . Using the value of  $V_b$  given by equation (56) and that of R assumed in equation (52), we find that we must have

$$\begin{split} -\pi\rho abce^3x \left(\mathfrak{c}_{11}x^4 + \mathfrak{c}_{22}y^4 + \mathfrak{c}_{33}z^4 + \mathfrak{c}_{12}x^2y^2 + \mathfrak{c}_{31}z^2x^2 + \mathfrak{c}_{23}y^2z^2 + \mathfrak{d}_1x^2 + \mathfrak{d}_2y^2 + \mathfrak{d}_3z^2 + \mathfrak{d}_4\right) \\ = -\pi\rho abc\theta e^3\frac{1}{4}\frac{x}{a^2} \left( \mathfrak{U}\frac{x^4}{a^8} + \mathfrak{M}\frac{y^4}{b^8} + \mathfrak{N}\frac{z^4}{c^8} + 2\mathfrak{I}\frac{y^2z^2}{b^4c^4} + 2\mathfrak{m}\frac{z^2x^2}{c^4a^4} \right. \\ \left. + 2\mathfrak{m}\frac{x^2y^2}{a^4b^4} + 2\left(\mathfrak{p}\frac{x^2}{a^4} + \mathfrak{q}\frac{y^2}{b^4} + \mathfrak{r}\frac{z^2}{c^4}\right) + \mathfrak{s}\right). \end{split}$$

On equating coefficients we obtain

$$\mathfrak{c}_{11} = \frac{1}{4} \frac{\theta}{a^{10}} \mathfrak{L}; \qquad \mathfrak{c}_{22} = \frac{1}{4} \frac{\theta}{a^2 b^8} \mathfrak{R}; \qquad \mathfrak{c}_{33} = \frac{1}{4} \frac{\theta}{a^2 c^8} \mathfrak{N}, \dots$$
(73)

$$\mathfrak{c}_{23} = \frac{1}{2} \frac{\theta}{a^2 b^4 c^4} \mathfrak{l} ; \qquad \mathfrak{c}_{31} = \frac{1}{2} \frac{\theta}{a^6 c^4} \mathfrak{m} ; \qquad \mathfrak{c}_{12} = \frac{1}{2} \frac{\theta}{a^6 b^4} \mathfrak{n} , \dots$$
 (74)

$$\mathfrak{d}_1 = \frac{1}{2} \frac{\theta}{\alpha^6} \mathfrak{p} ; \qquad \mathfrak{d}_2 = \frac{1}{2} \frac{\theta}{\alpha^2 b^4} \mathfrak{q} ; \qquad \mathfrak{d}_3 = \frac{1}{2} \frac{\theta}{\alpha^2 c^4} \mathfrak{r}, \qquad (75)$$

$$\mathfrak{d}_4 = \frac{1}{4} \frac{\theta}{a^2} \mathfrak{s}. \qquad (76)$$

These equations, in addition to those found for the first- and second-order terms in the previous paper, express the condition that the third-order figure (72) shall be a possible figure of equilibrium.

15. On substituting the values of  $\mathfrak{c}_{11}, \mathfrak{c}_{12} \dots \mathfrak{c}_{33}$  which have been obtained in § 12 into the six equations (73) and (74), we obtain a system of six equations from which it is possible to determine the six unknowns  $\mathfrak{L}$ ,  $\mathfrak{M}$ ,  $\mathfrak{N}$ ,  $\mathfrak{l}$ ,  $\mathfrak{m}$ ,  $\mathfrak{n}$ . The solution is actually effected in § 17 below.

If we substitute the three values of  $\mathfrak{d}_1$ ,  $\mathfrak{d}_2$  and  $\mathfrak{d}_3$  obtained in §12 (equations (62)-(64)) into the three equations (75), we obtain three equations which can be written in the form:—

$$\mathfrak{p}\left(\frac{1}{2}\frac{\theta}{a^6} + \frac{3}{4}\int_0^\infty \frac{\mathbf{A}d\lambda}{\Delta \mathbf{A}^2} - \frac{1}{2}\int_0^\infty \frac{d\lambda}{\Delta \mathbf{A}^3}\right) + \frac{1}{4}\mathfrak{q}\int_0^\infty \frac{\mathbf{B}d\lambda}{\Delta \mathbf{A}^2} + \frac{1}{4}\mathfrak{r}\int_0^\infty \frac{\mathbf{C}d\lambda}{\Delta \mathbf{A}^2} = \delta_1 - 2\int_0^\infty \frac{\mathbf{G}}{\Delta \mathbf{A}^2}d\lambda, \quad . \quad (77)$$

$$\frac{3}{4}\mathfrak{p}\int_{0}^{\infty}\frac{\mathbf{A}d\lambda}{\Delta\mathbf{A}\mathbf{B}}+\mathfrak{q}\left(\frac{1}{2}\frac{\theta}{a^{2}b^{4}}+\frac{1}{4}\int_{0}^{\infty}\frac{\mathbf{B}d\lambda}{\Delta\mathbf{A}\mathbf{B}}-\frac{1}{2}\int_{0}^{\infty}\frac{cd\lambda}{\Delta\mathbf{A}\mathbf{B}^{2}}\right)+\frac{1}{4}\mathfrak{r}\int_{0}^{\infty}\frac{\mathbf{C}d\lambda}{\Delta\mathbf{A}\mathbf{B}}=\delta_{2}-2\int_{0}^{\infty}\frac{\mathbf{G}}{\Delta\mathbf{A}\mathbf{B}}d\lambda,\tag{78}$$

$$\frac{3}{4}\mathfrak{p}\int_{0}^{\infty}\frac{\mathbb{A}d\lambda}{\Delta AC} + \frac{1}{4}\mathfrak{q}\int_{0}^{\infty}\frac{\mathbb{B}d\lambda}{\Delta AC} + \mathfrak{r}\left(\frac{1}{2}\frac{\theta}{a^{2}c^{4}} + \frac{1}{4}\int_{0}^{\infty}\frac{\mathbb{C}d\lambda}{\Delta AC} - \frac{1}{2}\int_{0}^{\infty}\frac{d\lambda}{\Delta AC^{2}}\right) = \delta_{3} - 2\int_{0}^{\infty}\frac{G}{\Delta AC}d\lambda. \quad (79)$$

It will be seen that  $\mathfrak{p}$ ,  $\mathfrak{q}$ .  $\mathfrak{r}$  do not occur on the right-hand sides of these equations.

These equations are not, as might at first be thought, a system of three simple equations determining  $\mathfrak{p}$ ,  $\mathfrak{q}$ ,  $\mathfrak{r}$ . They will be found to be of the type known as "porismatic"\*; that is to say, equations which are inconsistent unless the coefficients satisfy a certain relation, and such that, when this relation is satisfied, the equations have an infinite number of solutions.

Let us, for brevity, write the equations in the form:—

$$k_{1}\mathfrak{p} + k'_{1}\mathfrak{q} + k''_{1}\mathfrak{r} = \mathfrak{Z}_{1}$$

$$k_{2}\mathfrak{p} + k'_{2}\mathfrak{q} + k''_{2}\mathfrak{r} = \mathfrak{Z}_{2}$$

$$k_{3}\mathfrak{p} + k'_{3}\mathfrak{q} + k''_{3}\mathfrak{r} = \mathfrak{Z}_{3}$$

$$(80)$$

Let us use also the abbreviated notation of the previous paper (p. 50), such that

$$c_1 = \int_0^\infty \frac{\lambda d\lambda}{\Delta \, \text{ABC}}, \qquad c_2 = \int_0^\infty \frac{\lambda d\lambda}{\Delta \, \text{A}^2 \text{C}}, \qquad c_3 = \int_0^\infty \frac{\lambda d\lambda}{\Delta \, \text{A}^2 \text{B}}.$$

Then, by simple transformations of the integrals, we obtain

$$k_{1} = \frac{1}{4\alpha^{2}} \left( \frac{2\theta}{a^{4}} - c_{2} - c_{3} \right), \qquad k'_{1} = \frac{1}{4b^{2}} c_{3}, \qquad k''_{1} = \frac{1}{4c^{2}} c_{2},$$

$$k_{2} = \frac{3}{4\alpha^{2}} c_{3}, \qquad k'_{2} = \frac{1}{4b^{2}} \left( \frac{2\theta}{\alpha^{2}b^{2}} - 3c_{3} - c_{1} \right), \qquad k''_{2} = \frac{1}{4c^{2}} c_{1},$$

$$k_{3} = \frac{3}{4\alpha^{2}} c_{2}, \qquad k'_{3} = \frac{1}{4b^{2}} c_{1}, \qquad k''_{3} = \frac{1}{4c^{2}} \left( \frac{2\theta}{\alpha^{2}c^{2}} - 3c_{2} - c_{1} \right),$$

$$(81)$$

With these values of the coefficients, it will be found that equations (71)-(73) of the previous paper reduce to

$$2k_{1}\alpha + 2k'_{1}\beta + 2k''_{1}\gamma = 0$$

$$2k_{2}\alpha + 2k'_{2}\beta + 2k''_{2}\gamma = 0$$

$$2k_{3}\alpha + 2k'_{3}\beta + 2k''_{3}\gamma = 0$$
, . . . . . . (82)

so that

$$\mathfrak{p}=2\alpha, \qquad \mathfrak{q}=2\beta, \qquad \mathfrak{r}=2\gamma, \ldots \ldots \ldots$$
 (83)

is a solution of equations (80), when  $\mathfrak{B}_1 = \mathfrak{B}_2 = \mathfrak{B}_3 = 0$ .

Without this detailed inspection of the equations, it could have been foreseen that this would necessarily be the case. For our general solution

$$\phi = eP + e^2Q + e^3R$$
, . . . . . . . (84)

<sup>\*</sup> See 'Hobson's Plane Trigonometry,' § 73, or Wolstenholme, 'Proc. London Math. Soc.,' vol. 4.

must cover all possible figures of equilibrium as far as the third order. One such figure is, however, known to be

$$\phi = e \cdot 0 + e^2 \cdot 0 + e^3 P$$
, . . . . . . . (85)

and the corresponding solution for  $\mathfrak{p}$ ,  $\mathfrak{q}$ ,  $\mathfrak{r}$  is that expressed by equations (83).

From equations (82), it follows at once that we must have

Indeed, it is now clear that this is precisely the equation which determined the existence of the point of bifurcation on the series of Jacobian ellipsoids.\*\*

If this were the only relation between the coefficients in equations (80), these equations could have no solution other than  $\mathfrak{p} = \mathfrak{q} = \mathfrak{r} = \infty$ . Let us, however, multiply the three equations (80) by the three minors of  $k''_1$ ,  $k''_2$ ,  $k''_3$  in the determinant of equation (86), and add. We obtain a relation of the type,

$$\mathfrak{p} \cdot 0 + \mathfrak{q} \cdot 0 + \mathfrak{r} \cdot 0 = \begin{pmatrix} k_1, & k'_1, & \mathfrak{K}_1 \\ k_2, & k'_2, & \mathfrak{K}_2 \\ k_3, & k'_3, & \mathfrak{K}_3 \end{pmatrix}, \quad \dots \quad (87)$$

and it is clear that these equations can now have a solution in which  $\mathfrak{p}$ ,  $\mathfrak{q}$ ,  $\mathfrak{r}$  are not all infinite if we have

It is only when this relation is satisfied that it is possible to continue our linear series of equilibrium configurations beyond the second order terms. When it is not satisfied, our third order solution (84) lapses back into the solution (85), namely  $\phi = e^3P$ , which is virtually the first order solution with  $e^3$  replacing e as parameter.

16. The relation (88) can be expressed in a much simpler form.

Independently of the values of  $\mathfrak{p}$ ,  $\mathfrak{q}$  and  $\mathfrak{r}$ , we have already seen (equation (71)) that we must have

<sup>\*</sup> As to the relation of this equation to the general theory, see § 36 of my previous paper.

On substituting the values for  $\mathfrak{d}_1$ ,  $\mathfrak{d}_2$  and  $\mathfrak{d}_3$  given by equations (62)-(64), and equating coefficients of  $\mathfrak{p}$ ,  $\mathfrak{q}$ ,  $\mathfrak{r}$  in equation (89) to zero, we obtain

$$3\mathbf{K}_{1} + \mathbf{K}_{2} + \mathbf{K}_{3} = 0.$$

$$3k_{1} + k_{2} + k_{3} = \frac{3}{2} \frac{\theta}{a^{6}}.$$

$$3k'_{1} + k'_{2} + k'_{3} = \frac{1}{2} \frac{\theta}{a^{2}b^{4}}.$$

$$3k''_{1} + k''_{2} + k''_{3} = \frac{1}{2} \frac{\theta}{a^{2}c^{4}}.$$

With the help of these relations equation (88) reduces quite simply to

$$\mathfrak{X}_{1}\left(\frac{3}{a^{4}}k'_{2}-\frac{1}{b^{4}}k_{2}\right)=\mathfrak{X}_{2}\left(\frac{3}{a^{4}}k'_{1}-\frac{1}{b^{4}}k_{1}\right). \qquad (90)$$

In this equation the coefficients of  $\mathfrak{F}_1$  and  $\mathfrak{F}_2$  depend only on a, b, c the semi-axes of the Jacobian ellipsoid, and so are fully known. The quantities  $\mathfrak{F}_1$ ,  $\mathfrak{F}_2$  however depend on the second-order coefficients L, M, N, ... p, q, r, s. These were calculated in the previous paper, but p, q, r, s could not be fully determined, since they were found to depend on a quantity n'', which measured the change in angular velocity This it was found impossible to evaluate so long as the investigation was confined to second-order terms. It now appears that equation (90) is in effect an equation determining n''. The equation is linear in n'', so that it gives only one value for n''. When n'' has this value we are on the true linear series, but if n'' has any other value our solution, when we try to extend it to third-order terms, degenerates into a solution of the type of (85), with which no progress can be made. Our plan, then, is to evaluate the terms which occur in equation (90) and so obtain the value of n''. On inserting this into the values of p, q, r, s which were obtained in the previous paper, we complete the solution as far as the second-order terms, and can then proceed to the stability criterion.

## Numerical Computations.

17. It is at once apparent that the evaluation of  $\mathfrak{c}_{11}$ ,  $\mathfrak{c}_{12}$ , ...,  $\mathfrak{d}_1$ ,  $\mathfrak{d}_2$ , ..., given by equations (58)–(67), can be made to depend on integrals of the same type as occurred in the previous paper, namely integrals defined by

$$J_{ABC...} = \int_0^\infty \frac{d\lambda}{\Delta ABC...}.$$

In addition to the integrals which were given in the previous paper,\* I have calculated the following values of additional integrals needed for the computation of third-order terms.

$J_{B^s} = 0.9637364,$	$J_{BC} = 1.392786,$	$J_{B^3C^2} = 2.024097,$
$J_{B^2C^3} = 2.948174,$	$J_{BC'} = 4.316064,$	$J_{C^5} = 6.336915,$
$J_{A^6} = 0.0001716853,$	$J_{A^{6}B} = 0.0006851396,$	$J_{A^5C} = 0.000942028,$
$J_{A^4B^2} = 0.002877084,$	$J_{A^4BC} = 0.004027127,$	$J_{A^4C'} = 0.005675881,$
$J_{A^2B^3} = 0.01256355,$	$J_{A^3B^2C} = 0.01783828,$	$J_{A^{\prime}BC^2} = 0.02547622,$
$J_{A^3C^3} = 0.0365761,$	$J_{A^2B^4} = 0.0565289,$	$J_{A^2B^3C} = 0.0811833,$
$J_{A^2B^2C^2} = 0.1172029,$	$J_{A^2BC^2} = 0.1698776,$	$J_{A^2C^4} = 0.2473229,$
$J_{AB^5} = 0.260331,$	$J_{AB^4C} = 0.377266,$	$J_{AB^3C^2} = 0.549771,$
$J_{AB^2C^3} = 0.802462,$	$J_{ABC^4} = 1.177387,$	$J_{AC^5} = 1.731910,$
$J_{B^{\epsilon}} = 1.221051,$	$J_{B^{5}C} = 1.781565,$	$J_{B^4C^2} = 2.621427,$
$J_{B^3C^3} = 3.837093,$	$J_{B^2C^4} = 5.679960,$	$J_{BC^5} = 8.391280,$
	$J_{C^6} = 12.448855,$	
$J_{A^7} = 0.0000434660,$	$J_{A^6B} = 0.000177533,$	$J_{A^{6}C} = 0.000245881,$
$J_{A^5B^2} = 0.000757892,$	$J_{A^5BC} = 0.00106671,$	$J_{A^5C^2} = 0.00151097,$
$J_{A^4B^3} = 0.00334922,$	$J_{A^4B^2C} = 0.00477536,$	$J_{A^4BC^2} = 0.00684621,$
$J_{A^4C^3} = 0.00986287,$	$J_{A^3B^4} = 0.0152016,$	$J_{A^8B^8C} = 0.0219023,$
$J_{A^3B^2C^2} = 0.0317157,$	$J_{A^3BC^3} = 0.0460906,$	$J_{A^3C^4} = 0.0672671,$
$J_{A^2B^5} = 0.0704673,$	$J_{A^2B^4C} = 0.102374,$	$J_{A^2B^8C^2} = 0.149566,$
$J_{A^2B^2C^8} = 0.218724,$	$J_{A^2BC^4} = 0.321581,$	$J_{A^2C^5} = 0.473857,$
$J_{AB^6} = 0.332181,$	$J_{AB^{5}C} = 0.485553,$	$J_{AB^4C^2} = 0.716300,$
$J_{AB^3C^3} = 1.04926,$	$J_{AB^2C^4} = 1.55682,$	$J_{ABC^5} = 2.30256,$
	$J_{AC^6} = 3.42068.$	

The first task is the evaluation of  $\mathfrak{c}_{11}$ ,  $\mathfrak{c}_{12}$ , ...,  $\mathfrak{c}_{33}$ . These quantities are connected by the three relations (68)–(70), so that only three of the six quantities need have been calculated. I have, however, calculated four coefficients, namely,  $\mathfrak{c}_{12}$ ,  $\mathfrak{c}_{13}$ ,  $\mathfrak{c}_{22}$  and  $\mathfrak{c}_{33}$  quite independently, the object being to obtain a check on the accuracy of the computations. In this way a check is obtained at every step of the computations.

In each case the error was one of printing only, and did not enter into the computations. The whole table given in the previous paper was recomputed before extending it for purposes of the present paper.

<sup>\*</sup> The following are true values of integrals which were incorrectly given in the previous paper:—  $J_{\text{BCC}} = 1.3419631, \qquad J_{\text{AABCC}} = 0.09510324, \qquad I_{\text{CCCC}} = 0.4781180.$ 

The values obtained were

$$\mathfrak{c}_{13} = -0.0003503 \mathbb{L} + 0.0035301 \mathbb{M} - 0.0295936 \mathbb{N}$$

$$-0.0024284 \mathbb{L} + 0.0074994 \mathbb{m} - 0.0010296 \mathbb{m} + 0.0044353, \qquad (92)$$

$$\mathfrak{c}_{22} = 0.0001010\mathfrak{L} + 0.0126532\mathfrak{M} + 0.0153304\mathfrak{N} -0.0250819\mathfrak{I} + 0.0010344\mathfrak{m} -0.0017407\mathfrak{n} -0.0015791, \qquad (93)$$

$$\mathfrak{c}_{33} = 0.0001361 \mathcal{L} + 0.0062287 \mathcal{H} + 0.0353141 \mathcal{N} -0.0261575 \mathcal{I} -0.0035230 \mathfrak{m} + 0.0007874 \mathfrak{n} -0.0016798. \qquad (94)$$

Two values of  $\mathfrak{r}_{23}$  can now be deduced from equations (69) and (70) respectively. These are found to be

$$\mathfrak{c}_{23} = \frac{+0.0002337}{+0.0002343} \mathfrak{L} -0.047957 \mathfrak{M} -0.123015 \mathfrak{N} \\ +0.16424 \\ +0.16420 \mathfrak{l} -0.001361 \mathfrak{m} -0.001636 \mathfrak{m} -0.003242 \\ -0.001360 \mathfrak{m} -0.001636 \mathfrak{m} -0.003227.$$

The agreement of these values provides a check on the computations of the coefficients  $\mathfrak{r}_{12}$ , ..., and of the integrals from which they have been calculated.

In virtue of relations (73), equations (68)–(70) become

$$5\frac{\mathcal{L}}{a^4} + \frac{\mathfrak{n}}{b^4} + \frac{\mathfrak{m}}{c^4} = 0, \dots$$
 (95)

$$3\frac{\mathfrak{M}}{b^4} + \frac{3\mathfrak{n}}{a^4} + \frac{\mathfrak{l}}{c^4} = 0, \dots$$
 (96)

$$3\frac{\mathcal{M}}{c^4} + \frac{3\mathfrak{m}}{a^4} + \frac{\mathfrak{l}}{b^4} = 0, \qquad (97)$$

while relations (73) and (74), of which only three are now independent, may be represented by

$$\mathfrak{c}_{22} - \frac{1}{4} \frac{\theta}{a^2 b^8} \mathfrak{M} = 0.$$
 . . . . . . . (100)

On substituting for  $\mathfrak{r}_{12}$ ,  $\mathfrak{r}_{13}$ , and  $\mathfrak{r}_{22}$  from equations (91)–(98), these become six linear equations for  $\mathfrak{U}$ ,  $\mathfrak{M}$ ,  $\mathfrak{N}$ ,  $\mathfrak{l}$ ,  $\mathfrak{m}$ , and  $\mathfrak{n}$ .

The solution of these equations is found to be

$$\mathfrak{U} = -12.6275,$$
  $\mathfrak{M} = -0.0307056,$   $\mathfrak{N} = -0.0044636,$   $\mathfrak{I} = -0.0116194,$   $\mathfrak{m} = 0.42602,$   $\mathfrak{n} = 1.15365.$ 

These values have been checked by insertion, not only in the six equations from which they were directly derived, but also in the remaining equations (73) and (74).

We now have all the material necessary for the evaluation of  $\mathfrak{B}_1$ ,  $\mathfrak{B}_2$  and  $\mathfrak{B}_3$ , which, it will be remembered, are the right-hand members of equations (77)–(79) respectively. These have been computed independently, and I found

$$\mathfrak{K}_1 = -0.0016803 + 0.228894n'',$$
 $\mathfrak{K}_2 = +0.0026780 - 0.301110n'',$ 
 $\mathfrak{K}_3 = +0.0023739 - 0.385644n''.$ 

These values ought to satisfy  $(cf. \S 16)$ 

$$3\mathbb{K}_1 + \mathbb{K}_2 + \mathbb{K}_3 = 0$$

in place of which I find

$$3\mathbf{B}_1 + \mathbf{B}_2 + \mathbf{B}_3 = 0.000011 - 0.00007n'',$$

but the error is no greater than might reasonably be expected in view of the very large number of operations in each computation.\*

The coefficients in equation (90) are found to be

$$\frac{3}{a^4}k'_2 - \frac{1}{b^4}k_2 = 0.0058753, \qquad \frac{3}{a^4}k'_1 - \frac{1}{b^4}k_1 = 0.00024949,$$

so that the equation itself becomes

$$5.8753(-0.0016803 + 0.228894n'') = 0.24949(0.0026780 - 0.301110n''),$$

and the solution is found to be

$$n'' = 0.007423.$$

Completion of Second Order Solution.

18. On substituting the value just obtained for n'' into the values for p, q, r, s, found in the previous paper (§ 34), I find,

$$p = 3.124954,$$

$$q = -0.103164,$$

$$r = -0.015236,$$

$$s = -0.256962,$$

thus completing the figure to the second-order terms.

\* Each of the quantities  $\mathbf{R}_1$ ,  $\mathbf{R}_2$ ,  $\mathbf{R}_3$  has been computed by expressing it as a sum of integrals of the type tabulated on p. 21. The first term in  $\mathbf{R}_1$ , namely  $13\frac{1}{8}\kappa\alpha^2a^{-4}\mathbf{J}_{AAA}$ , may be thought of as a typical term. Each of the quantities  $\mathbf{R}_1$ ,  $\mathbf{R}_2$ ,  $\mathbf{R}_3$  consisted of 326 such terms, so that  $3\mathbf{R}_1 + \mathbf{R}_2 + \mathbf{R}_3$  is a sum of 978 such terms, each of which, it must be remembered, is evaluated by a fairly lengthy series of computations.

The corresponding rotation is given by

$$\frac{\omega^2}{2\pi\rho} = n + e^2 n'' = 0.14200 + 0.007423e^2.$$

We notice at once that  $\omega$  increases as we pass along the pear-shaped series, whereas in Sir G. Darwin's solution  $\omega$  was found to decrease. Thus the present solution diverges in essentials from that of Darwin.

On the other hand the present solution is similar to that for rotating cylinders\* in which the rotation was also found to increase as we passed along the pear-shaped series, and as we shall now see, the increase is at a very similar rate.

Our present figure, as far as the first order of small quantities, is

$$\frac{x^2}{3.55} + \frac{y^2}{0.664} + \frac{z^2}{0.424} + e\left(-0.079x^3 + 0.127xy^2 + 0.106xz^2 + 0.142x\right) = 1,$$

while the cylindrical figure, on replacing the parameter  $10^{8/2}\theta$  used in the second half of the two-dimensional investigation by e, was found to be

$$\frac{x^2}{5} + \frac{y^2}{0.555} + e\left(-0.063x^3 + 0.190xy^2 + 0.211x\right) = 1.$$

A comparison of these two figures shows that the two e's may be taken to be very approximately the same. As regards angular velocity, the value in the present three-dimensional problem has been found to be

$$\frac{\omega^2}{2\pi\rho} = n + n''e^2 = 0.14200 \ (1 + 0.05227e^2),$$

while that in the two-dimensional problems wast

$$\frac{\omega^2}{2\pi\rho} = \frac{3}{8} + \frac{8.625}{448}e^2 = 0.3750 \ (1 + 0.0513e^2).$$

Thus, in so far as it is possible to compare the three-dimensional problem with its two-dimensional analogue, we may say that the two rotations are in very close agreement.

## Calculation of the Moment of Inertia.

- 19. We know that the pear-shaped figure will be stable or unstable according as the angular momentum increases or decreases as we pass from the critical Jacobian ellipsoid along the series of pear-shaped figures.
  - \* "On the Equilibrium of Rotating Liquid Cylinders," 'Phil. Trans.,' A, vol. 200 (1902), p. 67.
- † I have recently repeated the calculations of the two-dimensional problem as far as the third order of small quantities, including the evaluation of  $\omega^2$ , and find that the numbers given originally for the figure and angular velocity are absolutely correct. See, however, § 21 below.

The moment of inertia of the pear-shaped figure about the axis of rotation, say  $Mk^2$ , will be given by

$$Mk^2 = \iiint \rho (x^2 + y^2) dx dy dz$$

where the integral is taken throughout the volume of the pear-shaped figure. We have, by our choice of the coefficient s, ensured that the volume of the pear-shaped figure shall remain always equal to that of the original ellipsoid, so that we have

$$\mathbf{M} = \frac{4}{3} \pi \rho abc,$$

and therefore

$$k^{2} = \frac{3}{4\pi} \iiint (x^{2} + y^{2}) \frac{dx \, dy \, dz}{abc} \, . \quad . \quad . \quad . \quad . \quad (101)$$

Let us transform to co-ordinates x', y', z', given by

$$x' = \frac{x}{a}, \quad y' = \frac{y}{b}, \quad z' = \frac{z}{c}. \quad (102)$$

so that the critical Jacobian ellipsoid is reduced to a sphere of unit radius, and the pear-shaped figure is reduced to a distorted sphere. With this transformation, equation (101) becomes

$$k^{2} = \frac{3}{4\pi} \iiint (a^{2}x'^{2} + b^{2}y'^{2}) du' dy' dz', \quad . \quad . \quad . \quad . \quad (103)$$

where the integral is taken throughout the figure bounded by the surface

$$x'^{2} + y'^{2} + z'^{2} - 1 + e \frac{x'}{a} \left( a \frac{x'^{2}}{a^{2}} + \beta \frac{y'^{2}}{b^{2}} + \gamma \frac{z'^{2}}{c^{2}} + \kappa \right)$$

$$+ \frac{1}{4} e^{2} \left[ \frac{Lx'^{4}}{a^{4}} + \frac{My'^{4}}{b^{4}} + \dots + s \right] = 0. \quad . \quad . \quad . \quad . \quad . \quad (104)$$

Let  $r^2$  be written for  $x'^2 + y'^2 + z'^2$ , and let us further put

$$x' = rx$$
,  $y' = ry$ ,  $z' = rz$ ,

so that x, y, z, are co-ordinates on a sphere of unit radius. Equation (104) becomes

$$r^{2} - 1 + er^{3} \frac{\mathbf{x}}{a} \left( a \frac{\mathbf{x}^{2}}{a^{2}} + \beta \frac{\mathbf{y}^{2}}{b^{2}} + \gamma \frac{\mathbf{z}^{2}}{c^{2}} \right) + er \frac{\mathbf{x}\kappa}{a}$$

$$+ \frac{1}{4} e^{2} \left[ \frac{\mathbf{L} \mathbf{x}^{4} r^{4}}{a^{4}} + \frac{\mathbf{M} \mathbf{y}^{4} r^{4}}{b^{4}} + \dots + s \right] = 0. \qquad (105)$$

Let us suppose that r, the radius vector to the boundary of this distorted unit sphere is given by

$$r = 1 + ef + e^2g + e^3h + \dots$$

On substituting this value for r into equation (105) and equating the coefficients of e and  $e^2$ , we obtain

$$2f + \frac{x}{a} \left[ a \frac{x^2}{a^2} + \beta \frac{y^2}{b^2} + \gamma \frac{z^2}{c^2} + \kappa \right] = 0 \quad . \quad . \quad . \quad . \quad (106)$$

$$f^{2} + 2g + f\frac{x}{a} \left[ 3\left(\alpha \frac{x^{2}}{a^{2}} + \beta \frac{y^{2}}{b^{2}} + \gamma \frac{z^{2}}{c^{2}}\right) + \kappa \right] + \frac{1}{4} \left[ \frac{Lx^{4}}{a^{4}} + \frac{My^{4}}{b^{4}} + \dots + s \right] = 0. \quad (107)$$

If  $d\Omega$  is an element of solid angle, equation (103) may be written in the form

$$k^{2} = \frac{3}{4\pi} \iiint (a^{2}x^{2} + b^{2}y^{2}) r^{4} dr d\Omega,$$
  
=  $\frac{3}{20\pi} \iint (a^{2}x^{2} + b^{2}y^{2}) (1 + 5ef + 5e^{2}g + 10e^{2}f^{2}) d\Omega.$ 

Hence we find that  $k^2$  may be written in the form  $k_0^2 + \Delta k^2$ , where, as far as  $e^2$ ,

$$\Delta k^2 = \frac{3}{4\pi} \iint (a^2 x^2 + b^2 y^2) (g + 2f^2) d\Omega.$$

The integral is here taken over the sphere of unit radius, and so can be easily evaluated. Carrying out the necessary computations, I find

$$k_0^2 = \frac{1}{5} (a^2 + b^2) = 0.844105.$$
  
 $\Delta k^2 = -0.079156e^2.$ 

Thus the moment of inertia is given by

$$Mk^2 = 0.844105M (1 - 0.09378e^2)$$

20. This again differs from Sir G. Darwin's result, in which it will be remembered it was found that the moment of inertia of the pear increased as  $e^2$  increased. But we shall now see that the difference between the two results agrees exactly with what was to be expected from the different values of n'' used in our two solutions.

Sir G. Darwin chose his parameter e (which I shall denote by  $e_{\rm D}$ ) in such a way that the longest radius vector of the pear-shaped figure was a (1+0.1482 $e_{\rm D}$ ). In my solution, the longest radius vector is found to be a (1+0.1309 $e_{\rm J}$ ), where  $e_{\rm J}$  denotes my parameter e. Hence I find as the relation between our parameters

$$e_{\rm D} = 0.8833 e_{\rm J}$$
.

Darwin's rotation was given by

$$\frac{\omega^2}{2\pi\rho} = 0.14200 \left(1 - 0.1443066 e_{\rm D}^2\right) = 0.14200 \left(1 - 0.11259 e_{\rm J}^2\right).$$

The general solution, apart from special values for the rotation, is such that, in my notation,

$$\frac{\omega^2}{2\pi\rho} = n + e_{\rm J}^2 n'' = 0.14200 \left( 1 + \frac{n''}{0.14200} e_{\rm J}^2 \right).$$

Hence I find that Darwin's solution ought to coincide with the solution obtained in my previous paper on assigning to n'' a value  $n''_{D}$  given by

$$n''_{\rm D} = -0.015988.$$

The solution given in the present paper, which is believed to give a true figure of equilibrium, is derived from the general solution by assigning to n'' a value  $n''_{J}$  given by

$$n''_{\rm J} = +0.007423.$$

In my previous paper, it was shown that there was, so far as second-order terms only were concerned, a doubly infinite series of figures of equilibrium, and it was found that these could be defined in terms of two independent parameters, e and  $\xi$ , where  $\xi$  was the same thing as  $e_J^2n''$ . It accordingly appears that any figure of Darwin's series differs from my figure of equilibrium having the same value of e, through his  $\xi$  being different from mine. The excess of my  $\xi$  over his will be

$$\zeta_{J-D} = e_J^2 (n''_J - n''_D) = +0.023411e^2.$$

It is readily seen that the increase in the moment of inertia over that of the critical Jacobian, which has been called  $\Delta k^2$ , will be a linear function of  $\hat{\zeta}$  and  $e^2$ , say

$$\mu \xi + n e_{\rm J}^2$$
,

Hence the excess of my angular momentum over that of Darwin, will be

$$\mu \hat{\zeta}_{J-D}$$
.

The value of  $\mu$  is easily obtained by allowing  $e^2$  to vanish in the analysis given on p. 72 of my previous paper. The quantity  $\mu$  then appears as the rate of increase of  $k^2$  as we pass along the Jacobian series of ellipsoids. The general value of  $k^2$ , in the notation there used,\* is

$$k^{2} = \frac{1}{5} (a'^{2} + b'^{2}) = \frac{1}{5} a^{2} (1 - 12.71347 \xi) + \frac{1}{5} b^{2} (1 + 9.20894 \xi),$$

whence

$$\mu = \frac{\partial (k^2)}{\partial \xi} = -7.84851.$$

The excess of my value of  $k^2$  over that of Darwin ought accordingly to be

$$\mu \dot{\zeta}_{J-D} = -0.183060 e_J^2.$$

\* I have changed the sign of  $\zeta$ , which, by an oversight, had been taken with the opposite sign in my formulæ as printed in the previous paper.

My value of  $\Delta k^2$  having been seen to be  $-0.079156e_J^2$ , it follows that DARWIN'S ought to be

$$\Delta k^2 = 0.10390 e_{\rm J}^2 = 0.13317 e_{\rm D}^2$$

so that his value of  $k^2$  as deduced from my calculations ought to be

$$k^2 = 0.8441 (1 + 0.15777 e_D^2).$$

In point of fact the value actually given by DARWIN was

$$k^2 = 0.8441 (1 + 0.157786e_D^2).$$

It appears, then, that Darwin's moment of momentum agrees exactly with mine, as it ought, except for the difference introduced by the different values we have taken for n''. But, besides showing this, the calculations just given provide a check on the accuracy of the computations of both of us. Although our figures, as far as the second order, have been calculated by very widely different methods, their moments of momentum have been found to agree very closely.\*

21. The moment of momentum in the cylindrical problem was announced in my two-dimensional paper to increase with increasing  $e^2$ .

On repeating the computations of this paper, I find that the coefficients in the equation of the surface were correctly given, but the final computation of  $k^2$  was erroneous.† The corrected formula becomes

$$k^2 = k_o^2 (1 - 0.1679e^2).$$

22. We have now found for the pear-shaped figure of equilibrium,

$$\frac{\omega^2}{2\pi\rho} = 0.14200 \ (1 + 0.05227 e^2)$$

$$k^2 = 0.8441 (1 - 0.09378e^2)$$

† The error is in the very last stage of all; the value of  $\frac{1}{2}\gamma$  on p. 95 ought to read

$$\frac{1}{2}\gamma = 20 \cdot 25\alpha^6 - 118 \cdot 93\alpha^4 + 41 \cdot 071\alpha^2 + 229 \cdot 51,$$

and this leads to the formula

$$k^2 = k_0^2 (1 - 167.88\theta^2) = k_0^2 (1 - 0.16788e^2).$$

I have also calculated  $k^2$  by the method of § 19 of the present paper, and found

$$k^2 = k_0^2 (1 - 0.16791e^2),$$

<sup>\*</sup> It may perhaps be added that before I had discovered this check on my computations, I had calculated the mass of my pear-shaped figure by direct integration, using the method of §19. The total mass ought of course to come to exactly M. I find that the terms in  $\alpha^2$ ,  $\alpha\beta$ ... result in an increase of mass  $0.0689519 \text{M}e^2$ , while those in L, M, N ... s balance this with a decrease  $-0.0689514 \text{M}e^2$ .

It follows that the moment of momentum M is given by

$$\mathbf{M} = \mathbf{M}_0 (1 - 0.06765e^2).$$

Thus  $\mathbf{M} < \mathbf{M}_0$ , so that the moment of momentum decreases as we pass along the series of pear-shaped figures, and this series is therefore unstable.

### SUMMARY AND DISCUSSION OF RESULTS.

23. Throughout the present paper, and my previous paper on the same subject, the critical Jacobian ellipsoid which bifurcates into the pear-shaped series of figures of equilibrium, has been taken to be

$$f \equiv \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} - 1 = 0.$$

Any adjacent figure, whether of equilibrium or not, may be supposed to be

$$f + \phi = 0$$

where  $\phi$  is a function of x, y, z in which the coefficients are numerically small. For special values of  $\phi$ , this figure will be one of equilibrium. So long as we consider only figures which differ infinitesimally from f = 0, all the possible figures of equilibrium form a linear series, and  $\phi$  is of the form

$$\phi = eP$$
, . . . . . . . . (108)

where P is a function of x, y, z and e is a parameter which must be so small that  $e^2$  can be neglected.

In the previous paper it was shown that as soon as  $e^2$  is taken into account, there must be supposed to be a doubly infinite series of figures of equilibrium. The general form of  $\phi$  is

$$\phi = eP + e^2Q + \xi Q^1 \quad . \quad (109)$$

where  $\xi$  is a second parameter of the same order of magnitude as  $e^2$ , but capable of varying quite independently of  $e^2$ . The value of  $\frac{\omega^2}{2\pi\rho}$  for this figure of equilibrium is greater by  $\xi$  than the value for the critical Jacobian. The possible figures of equilibrium may be thought of as lying inside a rectangle having e,  $\xi$  as rectangular co-ordinates.

In the present paper I have carried the investigation as far as  $e^3$ , and find that the value of  $\phi$  as far as third-order terms must be of the form

$$\phi = eP + e^2Q + \xi Q^4 + e^3(R + KP) . . . . . . . (110)$$

where R is a new function of x, y, z and K is a constant. At first sight K appears to be at our disposal, for if we replace the parameter e by a new parameter  $e + \theta e^3$ , we can

vary K as much as we please. But on examining the problem in detail it is found that K is always infinite except for one special value of  $\xi$ . For this special value of  $\xi$  we can eliminate K altogether by a new choice of parameter. But for other values of  $\xi$ , our solution is only valid if  $e^3$ K is small, and, replacing  $e^3$ K by a new parameter  $e^1$ , the solution reduces to

$$\phi = 0 \cdot P + 0 \cdot Q + e^{1}P$$

and so returns to the original first-order solution (108).

Thus, except for one special value of  $\xi$ , it is impossible to carry the linear series outside the second order rectangle; if we attempt to do so, the solution keeps lapsing back into the first-order solution.

In the previous paper I gave reasons for believing that Sir G. Darwin, in his well-known investigation of this problem, had introduced a spurious equation of equilibrium. This extra equation could only be satisfied by assigning to  $\xi$  a special value, namely

$$\xi = -0.015988e^2$$
.

Sir G. Darwin accordingly gave this value to  $\xi$ , so that the value of  $\omega^2$  decreased on passing along his series of pear-shaped figures, and, assuming this value for  $\xi$ , he showed his series to be stable.

But the investigation of the previous paper showed that there was no need to assign this special value to  $\xi$ , and the present investigation has further shown that with this value of  $\xi$  it is impossible to extend the series beyond second-order terms at all. There is only one value of  $\xi$  which leads to a real linear series of configurations, and this is shown in the present paper to be

$$\xi = +0.007423e^2$$
.

Thus as we pass along the true linear series  $\omega^2$  continually increases. The angular momentum is however found to decrease, so that the pear-shaped figure is shown to be unstable.

24. The amount of computation involved in the problem has proved to be very great, and as the whole question of stability or instability depends on the sign of a single term at the end of all this computation, the question of numerical accuracy becomes one of great importance.

The difference between my second-order figure and that of DARWIN arises solely from the difference in the value of  $\xi$ . The moment of inertia of such figures is a linear function of  $\xi$ , and a very simple calculation gives the rate at which it ought to vary with  $\xi$ . Allowing for this difference in  $\xi$ , I find that my computations give for the moment of inertia of DARWIN's figure (in terms of DARWIN's parameter  $e_D$ ),

$$Mk_0^2(1+0.15777e_D^2),$$

while Darwin calculated as the value of the same quantity

$$Mk_0^2(1+0.157786e_{D}^2).$$

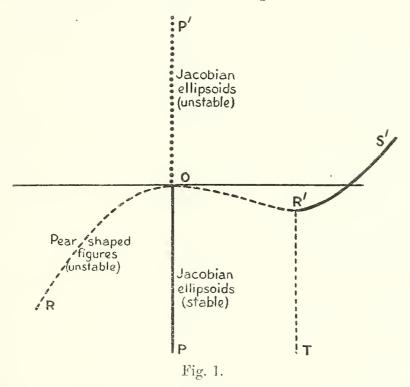
Since two independent sets of computations, conducted by entirely different methods, have been found to lead to precisely the same result, it seems highly probable that this result is accurate. The agreement just mentioned may reasonably be regarded as guaranteeing the accuracy of all the second-order computations, both of Darwin and myself.

The actual criterion of stability, however, depends on the value assigned to  $\zeta$ , and since this depends in turn on the third-order terms, no check by comparison with Darwin's work is possible. Some support is given to my value of  $\zeta$  by comparison with a parallel investigation of the "Equilibrium of Rotating Cylinders," which I published some years ago. Adjusting the parameters so that e shall have, as closely as possible, the same physical interpretation in the two problems, I find for the factor expressing the increase of  $\omega^2$  as we pass along the series of pear-shaped figures:

 $1+0.05227e^2$  for the three-dimensional problem,  $1+0.0513e^2$  for the two-dimensional problem.

Apart from this, the checks I have used in the present paper are such that I believe it would have been very difficult for any error to escape detection.

25. The main object of the paper is achieved as soon as the pear-shaped figure is shown to be unstable. It is at the same time of interest to examine the bearings of this result on the wider question of which it is a part.



In fig. 1 let PP' represent the series of Jacobian ellipsoids, the part PO (drawn thick) representing the stable part of the series, and the part OP' (drawn dotted) representing the unstable part, so that O is the point of bifurcation. Let a diagram be drawn about this line having the angular momentum always represented by the

vertical co-ordinates, so that for instance all systems, whether in equilibrium or not, which have the same angular momentum as the critical Jacobian ellipsoid, must be represented in the horizontal plane through O (this plane having as many "dimensions" as are necessary). In this diagram the pear-shaped series of figures will lie below this plane in the neighbourhood of O.

There are two a priori alternatives, represented on the right-hand and left-hand sides of fig. 1. In the first place, it is possible that after passing a certain distance OR' along the pear-shaped series with decreasing angular momentum, we come to a region R'S' in which the angular momentum again increases. Any horizontal line in the diagram ought, on the principle of stable and unstable configurations of equilibrium occurring alternately, to meet stable and unstable branches of the linear series alternately. Thus the branch R'S' ought to be stable, so that R' would be a point of bifurcation on this series, and the other series through R', say R'T, would be unstable.

The alternative possibility is that the pear-shaped series of figures proceeds continually downwards in the diagram, so that its angular momentum continually decreases.

26. Either of these two possibilities removes a difficulty to which Sir G. Darwin has drawn attention.\* In what is commonly referred to as Roche's problem an attempt is made to discover the other end of the pear-shaped series of figures, on the supposition that this other end represents two detached masses revolving about one another. Two such series of figures appear to exist†; in one the satellite is spheroidal except for tidal distortion, while in the other it is ellipsoidal. The former series has been shown to be stable, the latter unstable.

As the angular momentum decreases on passing along these series, the distance between the two masses also decreases until a point is reached at which the two series coalesce, the configuration of bifurcation being one in which the radius vector from the centre of the primary to that of the satellite is equal to 2.457 radii of the primary.‡ If the distance between the masses is decreased still further, the remaining configurations form an unstable series. Sir G. Darwin found a difficulty in the instability of this series, since he believed it to be the far end of the pear-shaped series which he thought stable. We now see, however, that this series may, without change of stability, join up with either the series TR' on the right-hand of our diagram, or the series RO on the left.

<sup>\* &#</sup>x27;Coll. Works,' III., pp. 515-524.

<sup>†</sup> Roche's problem has only been solved strictly by imposing sphericity on the primary and assuming the satellite to be infinitesimal. Sir G. Darwin's work ('Coll. Works,' III., p. 436), leaves little room for doubt that Roche's result may be extended in the way I have stated.

<sup>‡</sup> If the satellite is not infinitesimal, the radius vector depends on the ratio of the masses, but always lies between the narrow limits 2.457 and 2.514 times the radius of the primary (see DARWIN, loc. cit., p. 507).

27. We must now consider what motion is to be expected in a Jacobian ellipsoid which has reached the point of bifurcation at which instability sets in. Poincaré remarks\* that if the pear-shaped figure proved to be unstable, "la masse fluide devrait le dissoudre par un cataclysme subit."

After reaching the point O in our diagram, the mass cannot move along the pear-shaped series, since this would involve a decrease of angular momentum. It may be thought of as moving along the unstable branch OP' of the series of Jacobian ellipsoids for an infinitesimal time until some slight disturbance brings its instability into play.

Now of all the vibrations of this figure, it is known that one only is unstable, namely that corresponding to the third zonal harmonic of the ellipsoid. The initial motion of the figure must then be one in which the displacement at every point of the surface is proportional to the third zonal harmonic.

Thus the fluid begins by describing exactly the pear-shaped series, but as soon as the changes in angular momentum become appreciable, it leaves this series, and passes through a series of configurations represented in the region above O in fig. 1. These may at first be thought of as lying parallel to the pear-shaped series, but above O.

If there is a stable branch such as R'S' which ultimately passes above O, it is conceivable that the series of non-equilibrium configurations might ultimately coalesce with the series of equilibrium configurations R'S', and the motion would be continued along this series. In this case, M. Poincaré's "cataclysme subit" would consist in a jump from the stable series PO to the stable series R'S'.

Judging from the results of my parallel investigation on the configurations of rotating cylinders, this possibility does not seem at all likely. It is, I think, much more probable that the pear-shaped series lies like the series OR in my figure.

In this case also the liquid would move through a series of configurations which would initially be close to the series OR, but would get continually futher removed from configurations of equilibrium. The protuberance resulting from the initial third harmonic displacement would develop in a manner somewhat similar to that of the pear-shaped figure, but as the motion would necessarily be possessed of a considerable amount of kinetic energy, the phenomenon would be a dynamical and not a statical one. If the configuration represented at O in fig. 1 is the highest stable configuration possible for a single mass of liquid, this kinetic process can end in only one way, namely in the separation of the mass of liquid into two parts. As the third harmonic displacement develops, the region of the pear which moves with greatest velocity is known to be the extreme end of the protuberance. It is, therefore, natural to suppose that this part of the figure would be shot away first. Moreover as the departure from a figure of equilibrium is probably pretty pronounced before the separation takes place, it is likely that the mass in question will be shot away with a considerable velocity.

<sup>\*</sup> Letter to Sir G. DARWIN in the latter's 'Coll. Works,' III., p. 315.

After this projectile has left the main mass, the angular momentum of the latter, (measured of course per unit mass) will be reduced, and as the tidal influence of the newly-born satellite is gradually withdrawn, the primary may settle down to a state of stable equilibrium in which its figure is again that of a Jacobian ellipsoid. A cycle of processes such as this might very conceivably constitute the life-history of a rotating body after once it had passed the critical state represented by the point of bifurcation on the Jacobian series. There seems to be no reason why the protuberance should always develop at, and be shot off from, the same end of the Jacobian ellipsoid.

Thus it appears that the instability of the pear-shaped figure leads us to contemplate a series of processes of much the same nature as would have been expected if the pear had proved to be stable, except that we are now led to assign a much shorter time to these processes. The problem has ceased to be one of statics and has become one of dynamics; the phenomenon is no longer one of slow secular change but of collapse and explosion. The mechanism of planetary birth which is now suggested is so rapid that there need be no difficulty in supposing a planet to have been through the cycle several times; had the pear proved to be stable the cycle would probably have been so slow as to create a real difficulty.



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## II. On Periodic Disturbance of Level Arising from the Load of Neighbouring Oceanic Tides.

By K. Terazawa, Ri-Gakushi of the Imperial University of Tokyo.

Communicated by Sir Joseph Larmor, F.R.S.

Received April 17,—Read June 1, 1916.

## I. Introductory.

In his important observations on the lunar deflection of gravity, Dr. O. HECKER has pointed out that the force acting on the pendulum at Potsdam is a larger fraction of the moon's force when it acts towards the east or west than when it acts towards the north or south. Various explanations of this anomaly have been proposed; among them one, suggested by Prof. A. E. H. Love,\* is that a possible cause may perhaps be found in the attraction of the tide wave in the North Atlantic. Recently Prof. A. A. MICHELSON† has found a similar result in his arduous task, successfully achieved, of obtaining a continuous record of the lunar perturbation of a very long water-level at Chicago. Prof. Sir J. Larmor kindly suggested to me a query, whether the excess-pressure of the tide in the North Atlantic would affect much the measurement of water-level at Chicago, owing to the elastic depression of the earth's surface that it would produce.

In the present paper the calculation is undertaken in order to ascertain to what extent the consideration of tilting of the ground is important for the explanation of this geodynamical discrepancy, on the assumption that the earth consists of elastic matter of uniform density and of uniform invariable elastic constants, and that the North Atlantic may be represented roughly as a circular basin and that the tide in it is uniform or else elliptic. The curvature of the earth is neglected, which is, of course, admissible for a first estimation.

## II. General Formula.

The solution of the equation of equilibrium concerning an elastic body with plane boundary, otherwise extending to infinity, subject to certain boundary conditions,

<sup>\* &#</sup>x27;Some Problems of Geodynamics,' Cambridge (1911), p. 88.

<sup>† &#</sup>x27;The Astrophysical Journal,' vol. 39 (1914), p. 105.

has been obtained by Lamé and Clapeyron\* and by J. Boussinesq†; the former by making use of Fourier's theorem, and the latter by introducing several kinds of potential function. The solution for the case where the boundary condition is a normal pressure distributed symmetrically round a point on the surface and the body is free from bodily force is given by Prof. H. Lame‡ in a form of definite integral. I have tried to solve the problem, independently of Lame, and obtained the solution answering to any distribution of a normal pressure, from which the solution of Lame can be derived as a special case.§

For the present purpose let us confine our attention to the simplest case in which the boundary is subjected to a symmetrically distributed normal pressure. Take the centre of the area, in undisturbed state, on which the given normal pressure is distributed, as the origin of the co-ordinates, the inward normal to the undisturbed surface as the z-axis, and denote the distance of any point from the z-axis by r. Then corresponding to the normal pressure

$$\widehat{zz} = f(r), \qquad \dots \qquad \dots \qquad \dots \qquad \dots \qquad \dots \qquad \dots$$

given at the surface z = 0, we shall have the following expressions for the displacement components:—

$$u_{r} = -\frac{z}{2\mu} \int_{0}^{\infty} Z(k) e^{-kz} J_{1}(kr) dk$$

$$+ \frac{1}{2(\lambda + \mu)} \int_{0}^{\infty} Z(k) e^{-kz} J_{1}(kr) \frac{dk}{k}, \qquad (2)$$

$$n_{z} = -\frac{z}{2\mu} \int_{0}^{\infty} Z(k) e^{-kz} J_{0}(kr) dk$$

$$-\frac{\lambda + 2\mu}{2\mu (\lambda + \mu)} \int_{0}^{\infty} Z(k) e^{-kz} J_{0}(kr) \frac{dk}{k}, \qquad (3)$$

in which Z(k) stands for

$$Z(k) = k \int_0^a f(x) J_0(kx) x \, dx, \qquad (4)$$

 $\lambda$ ,  $\mu$  being Lamé's elastic constants,  $J_{\alpha}(x)$ ,  $J_{\alpha}(x)$  Bessel's functions of zeroth and first order, and  $\alpha$  the radius of loaded area.

Now, suppose the normal pressure (1) to arise entirely from the tidal loading in the North Atlantic basin, then the tidal loading would come into play to affect the water-level measurement at Chicago in two accounts: the one is the direct attraction of the material load, the other the deformation of the ground by the pressure

<sup>\* &#</sup>x27;Crelle's Journal,' vol. 7, p. 400 (1831).

<sup>† &#</sup>x27;Application des Potentiels . . . . , Paris (1885).

<sup>‡ &#</sup>x27;Lond. Math. Soc. Proc.,' vol. 34, p. 276 (1902).

<sup>§</sup> The solution, with numerous examples, will be published shortly elsewhere.

produced by that load. Dr. C. Chree,\* and afterwards more completely Prof. H. NAGAOKA,† find a formula, by using the formula obtained by Boussinesq, to calculate the deviation of the direction of gravity due to the attraction of a material load on the surface of the earth.

The same result can be attained, of course, from our solution. The expression for the vertical displacement at a point on the surface can be transformed into

$$(u_z)_0 = \frac{1}{2\pi} \cdot \frac{\lambda + 2\mu}{2(\lambda + \mu)\mu} \int_0^{2\pi} \int_0^a \frac{f(x)}{R'} x \, dx \, d\phi$$

by making use of Neumann's addition theorem for Bessel's functions, where R' stands for

$$R' = \sqrt{(r^2 - 2rx\cos\phi + x^2)}.$$

On the other hand, if we denote the attraction constant by  $\gamma$ , and gravity, prior to the application of the load, by g, then the gravitation-potential at a point on the unloaded surface due to the loading can be expressed by

$$\nabla_0 = \gamma \int_0^{2\pi} \int_0^a \frac{1}{g} \cdot \frac{f(x)}{R'} x \, dx \, d\phi,$$

provided the height of the loading material is negligibly small compared with the distance of the point under consideration from any point in the loaded area.

Comparing the above two expressions, we have

$$V_{0} = \frac{2\pi\gamma}{g} \cdot \frac{2\mu (\lambda + \mu)}{\lambda + 2\mu} (u_{z})_{0}.$$

Thus the direction of gravity becomes in consequence of the attraction of the loading material inclined to the vertical at the angle  $\psi$  which will be determined by

while its tilting effect is expressed by

$$\tan \phi = \left(\frac{\partial u_z}{\partial r}\right)_0. \qquad (6)$$

The total effect of the loading will thus be

$$\phi + \psi = \left(1 + \frac{2\pi\gamma}{g^2} \cdot \frac{2\mu(\lambda + \mu)}{\lambda + 2\mu}\right) \left(\frac{\partial u_z}{\partial r}\right)_0, \qquad (7)$$

in a close approximation.

\* 'Phil. Mag.,' V., 43, p. 177 (1897).

† Tôkyô, 'Sug. Buts. Kizi,' VI., p. 208 (1912).

## III. Uniform Loading.

Let  $\alpha$  be the radius of the loaded circle, h the height of the material loading, which is supposed to be uniform, and  $\rho$  its density, then we have to put

$$f(r) = -gh\rho \quad \text{for} \quad r < a,$$

$$= 0 \qquad ,, \quad r > a.$$
(8)

On this supposition, we get

$$Z(k) = -ahg_{\rho}J_{1}(ka),$$

therefore

$$u_{z} = \frac{ahg\rho z}{2\mu} \int_{0}^{\infty} e^{-kz} J_{0}(kr) J_{1}(ka) dk$$

$$+ \frac{ahg\rho (\lambda + 2\mu)}{2\mu (\lambda + \mu)} \int_{0}^{\infty} e^{-kz} J_{0}(kr) J_{1}(ka) \frac{dk}{k}, \qquad (9)$$

$$\left(\frac{\partial u_z}{\partial r}\right)_0 = -\frac{ahg\rho\left(\lambda + 2\mu\right)}{2\mu\left(\lambda + \mu\right)} \left[\int_0^\infty e^{-kz} J_1\left(kr\right) J_1\left(ka\right) dk\right]_{z=0}. \quad (10)$$

The other components of the displacement and those of stress can be expressed in similar forms. But it is unnecessary to write them down here as they are out of our present purpose.

The integrals required here cannot be evaluated in a very simple way. Some of them are closely connected to the magnetic potential due to a circular current, or to the velocity-potential and stream function of a circular vortex, and have been discussed by various authors. In his paper on the inductance of circular coils,\* Prof. Nagaoka has devised a comparatively simple method which may be applied to evaluate all the integrals needed for the calculation of the displacement and stress in the present problems. Let us follow his method and describe it here briefly.

Put

$$R = \sqrt{(a^2 + r^2 - 2ar\cos\theta)},$$

then by Neumann's addition theorem for Bessel's function we have

$$J_{1}(kr)J_{1}(ka) = \frac{1}{\pi} \int_{0}^{\pi} J_{0}(kR) \cos \theta \, d\theta,$$

$$J_{0}(kr)J_{1}(ka) = \frac{1}{\pi} \int_{0}^{\pi} \frac{a - r \cos \theta}{R} J_{1}(kR) d\theta.$$

Making use of these formulæ we obtain

$$\int_{0}^{\infty} e^{-kz} J_{1}(kr) J_{1}(ka) dk = \frac{1}{\pi} \int_{0}^{\pi} \frac{\cos \theta d\theta}{(R^{2} + z^{2})^{\frac{1}{2}}},$$

$$\int_{0}^{\infty} e^{-kz} J_{0}(kr) J_{1}(ka) dk = \frac{1}{\pi} \int_{0}^{\pi} \frac{a - r \cos \theta}{R^{2}} d\theta - \frac{z}{\pi} \int_{0}^{\pi} \frac{a - r \cos \theta}{R^{2} (R^{2} + z^{2})^{\frac{1}{2}}} d\theta,$$

$$\int_{0}^{\infty} e^{-kz} J_{0}(kr) J_{1}(ka) \frac{dk}{k} = \frac{1}{\pi} \int_{0}^{\pi} \frac{a - r \cos \theta}{R^{2}} (R^{2} + z^{2})^{\frac{1}{2}} d\theta - \frac{z}{\pi} \int_{0}^{\pi} \frac{a - r \cos \theta}{R^{2}} d\theta.$$

To find these integrals, put

$$\alpha = \left(\frac{2}{ar}\right)^{\frac{1}{3}}, \qquad \beta = \frac{\alpha^2 + r^2 + z^2}{6\alpha r}, \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (11)$$

$$e_1 = \frac{2\beta}{\alpha}, \qquad e_2 = \frac{1-\beta}{\alpha}. \qquad e_3 = -\frac{1+\beta}{\alpha}, \qquad \dots \qquad (12)$$

so that

$$e_3 < e_2 < e_1$$

$$e_1 + e_2 + e_3 = 0,$$

and change the integration variable from  $\theta$  to s by

$$\cos\theta = \alpha s + \beta,$$

then

$$\int_0^{\pi} \frac{\cos \theta}{(R^2 + z^2)^{\frac{1}{2}}} d\theta = \frac{\alpha^2}{2} \int_{e_3}^{e_2} \frac{(2s + e_1) ds}{\{4(s - e_1)(s - e_2)(s - e_3)\}^{\frac{1}{2}}}.$$

Put again

$$s = \mathcal{O}(u)$$
.

then, since s or  $\mathcal{P}(u)$  is real and lies between  $e_3$  and  $e_2$ ,  $s = e_3$  and  $s = e_2$  correspond to  $u = \omega_3$  and  $u = \omega_2$  respectively, if we take  $\mathcal{P}'(u)$  to be positive\*; where  $\omega_1$  and  $\omega_3$  denote the real and imaginary half-period and  $\omega_2 = \omega_1 + \omega_3$ . Thus

$$\int_0^\pi \frac{\cos\theta \, d\theta}{(\mathbf{R}^2 + z^2)^{\frac{1}{2}}} = \alpha^2 \int_{\omega_3}^{\omega_2} (\frac{1}{2}e_1 + \mathcal{O}(u)) \, du$$

$$= \alpha^2 \left(\frac{1}{2}e_1\omega_1 - \eta_1\right). \qquad (13)$$

For the evaluation of the other integrals, write

$$\mathscr{O}(v) = \frac{a^2 + r^2 - 2ar\beta}{2ara}. \quad . \quad (14)$$

<sup>\*</sup> If we assume  $\mathscr{P}'(u)$  to be negative, then  $s = e_3$  and  $s = e_2$  correspond to  $u = \omega_2$  and  $u = 2\omega_1 + \omega_3$  respectively. But the same result will, as a matter of course, be obtained after integration.

then we shall have

$$\int_{0}^{\pi} \frac{a - r \cos \theta}{R^{2} (R^{2} + z^{2})^{\frac{1}{2}}} d\theta = \frac{\alpha}{2a} \omega_{1} - \frac{r^{2} - \alpha^{2}}{4a^{2}r} \int_{\omega_{3}}^{\omega_{2}} \frac{du}{\varphi(v) - \varphi(u)},$$

$$\int_{0}^{\pi} \frac{a - r \cos \theta}{R^{2}} (R^{2} + z^{2})^{\frac{1}{2}} d\theta = \frac{2}{aa} (e_{1}\omega_{1} + \eta_{1}) - \frac{r^{2} - \alpha^{2}}{a^{2}r\alpha^{2}} \omega_{1} + \frac{r^{2} - \alpha^{2}}{a^{2}r\alpha^{2}} \int_{\omega_{3}}^{\omega_{2}} \frac{\varphi(v) - e_{1}}{\varphi(v) - \varphi(u)} du.$$

Now we have

$$\int_{\omega_{3}}^{\omega_{2}} \frac{\wp'(v) du}{\wp(v) - \wp(u)} = \left[ \log \frac{\sigma(u+v)}{\sigma(u-v)} - 2u\xi(v) \right]_{\omega_{3}}^{\omega_{2}}$$

$$= 2v\eta_{1} - 2\omega_{1}\xi(v) + 2m\pi i. \qquad (15)$$

Hence

$$\int_{0}^{\pi} \frac{\alpha - r \cos \theta}{R^{2} (R^{2} + z^{2})^{\frac{1}{2}}} d\theta = \frac{\alpha}{2\alpha} \omega_{1} - \frac{r^{2} - \alpha^{2}}{2\alpha^{2} r S'(v)} \{ v \eta_{1} - \omega_{1} \xi(v) + m \pi i \}, \quad . \quad . \quad (16)$$

$$\int_{0}^{\pi} \frac{\alpha - r \cos \theta}{\mathbf{R}^{2}} \left( \mathbf{R}^{2} + z^{2} \right)^{\frac{1}{2}} d\theta = \frac{2}{\alpha \alpha} \left( e_{1} \omega_{1} + \eta_{1} \right) - \frac{r^{2} - \alpha^{2}}{\alpha^{2} r \alpha^{2}} \omega_{1} + \frac{2}{\alpha^{2} r \alpha^{2}} \cdot \frac{g(v) - e_{1}}{g'(v)} \left\{ v \eta_{1} - \omega_{1} \xi(v) + m \pi i \right\}. \tag{17}$$

The term  $m\pi i$  enters because of the many-valued property of a logarithm. The actual value of m and  $\mathscr{G}'(v)$  will be determined by the following consideration.

From the definition of  $\mathcal{P}(v)$  and  $e_1$ ,  $e_2$ ,  $e_3$ , it follows immediately that

$$\mathscr{P}(v) - e_1 = -\frac{z^2 \alpha}{2ar},$$

$$\mathscr{P}(v) - e_2 = \frac{(a - r)^2 \alpha}{2ar},$$

$$\mathscr{P}(v) - e_3 = \frac{(a + r)^2 \alpha}{2ar},$$

$$e_2 < \mathscr{P}(v) < e_1.$$

accordingly

The last inequality shows that the value of v must be one of the following:—

(i.) 
$$v = (2n+1)\omega_1 + (2n'+\theta)\omega_3$$
  
(ii.)  $v = (2n+1)\omega_1 + (2n'+2-\theta)\omega_3$ , . . . (18)

where n and n' denote any integers, positive or negative, or zero, and  $\theta$  a positive number less than unity. To determine the value of m in the formulæ (16) (17) for

the value of v given in (i.) of (18), observe that the integral on the left-hand side of (15) and the function  $v_{\eta_1} - \omega_1 \xi(v)$  change their values continuously as  $\theta$  varies from 0 to 1, while m remains unchanged in this variation. In the limit as  $\theta \to 0$ , the value of the integral is nil and

 $2v_n - 2\omega_1 \xi(v) = 2n'\pi i$ 

and therefore we have

(i.) 
$$m = -n'$$
.

Similarly for the value of v given in (ii.) of (18), proceeding to the limit  $\theta \to 0$ , we find

(ii.) 
$$m = -(n'+1)$$
.

The value of  $\mathcal{P}'(v)$  will be obtained from

$$\mathscr{D}^{\prime 2}\left(v\right)=4\left[\mathscr{D}\left(v\right)\!-\!e_{\scriptscriptstyle 1}\right],\left[\mathscr{D}\left(v\right)\!-\!e_{\scriptscriptstyle 2}\right],\left[\mathscr{D}\left(v\right)\!-\!e_{\scriptscriptstyle 3}\right].$$

In the present case we have

$$\mathscr{P}'(v) = \pm i \frac{z(a^2 - r^2)}{2ar}.$$

It may easily be shown that the value of  $\mathscr{D}'(v)$  is a positive imaginary quantity for the value of v given in (i.) of (18) and a negative imaginary quantity for (ii.).

Therefore we have to take

$$S'(v) = +i \left| \frac{z(\alpha^2 - r^2)}{2\alpha r} \right|,$$

$$m = -n',$$

$$v = (2n+1) \omega_1 + (2n'+\theta) \omega_3;$$
(19)

and

for

 $\beta'(v) = -i \left| \frac{z(\alpha^2 - r^2)}{2\alpha r} \right|,$  m = -(n'+1),  $v = (2n+1) \omega_1 + (2n'+2-\theta) \omega_3;$ 

for

where  $0 < \theta < 1$ .

Lastly, one more integral which can be evaluated without the knowledge of elliptic functions is

$$\int_0^\pi \frac{a - r \cos \theta}{R^2} d\theta = \frac{\pi}{a} \text{ for } r < a,$$

$$= 0 ,, r > a.$$
(21)

Substituting these values of integrals in (9), we have

$$u_{z} = \frac{ahg\rho z}{2\mu} \left\{ \begin{bmatrix} \frac{1}{a}(r < a) \\ 0(r > a) \end{bmatrix} - \frac{\alpha z \omega_{1}}{2a\pi} + \frac{z(r^{2} - a^{2})}{2a^{2}r\pi\theta'(v)} [r\eta_{1} - \omega_{1}\xi(v)] \right\}$$

$$+ \frac{ahg\rho(\lambda + 2\mu)}{2\mu(\lambda + \mu)} \left\{ - \begin{bmatrix} \frac{z}{a}(r < a) \\ 0(r > a) \end{bmatrix} + \frac{2}{aa\pi} (e_{1}\omega_{1} + \eta_{1}) - \frac{r^{2} - a^{2}}{\pi a^{2}ra^{2}} \omega_{1} \right\}$$

$$+ \frac{2(r^{2} - a^{2})}{\pi a^{2}ra^{2}} \cdot \frac{\varphi(v) - e_{1}}{\varphi'(v)} [v\eta_{1} - \omega_{1}\xi(v)] \right\}$$

$$(22)$$

in which the simplest value of v, i.e., n = 0, n' = 0 in (i.) of (18) is taken as the representative.

At the surface it reduces simply to

$$(u_z)_0 = \frac{hg\rho(\lambda + 2\mu)}{2\mu(\lambda + \mu)\pi} \left\{ \frac{2}{\alpha} \left( \eta_1 + e_1\omega_1 \right) - \frac{r^2 - \alpha^2}{\alpha r \alpha^2} \omega_1 \right\}, \qquad (23)$$

where

$$\alpha = \left(\frac{2}{\alpha r}\right)^{\frac{1}{3}},$$

$$e_1 = \frac{a^2 + r^2}{3ar\alpha}, \qquad e_2 = -\frac{a^2 + r^2 - 6ar}{6ar\alpha}, \qquad e_3 = -\frac{a^2 + r^2 + 6ar}{6ar\alpha}.$$
 (24)

Similarly for the value of  $\left(\frac{\partial u_z}{\partial r}\right)_0$  we have

$$\left(\frac{\partial u_z}{\partial r}\right)_0 = -\frac{hg\rho\left(\lambda + 2\mu\right)}{2\mu\left(\lambda + \mu\right)\pi} \cdot a\alpha^2 \left(\frac{1}{2}e_1\omega_1 - \eta_1\right). \tag{25}$$

For practical purposes of calculation, it will be very convenient to transform the expressions into Jacobi's q series; q being defined by

$$q=e^{i\pi au}, \qquad au=rac{\omega_3}{\omega_1}.$$

After Weierstrass, if we put

$$l = \frac{(e_1 - e_3)^{\frac{1}{4}} - (e_1 - e_2)^{\frac{1}{4}}}{(e_1 - e_3)^{\frac{1}{4}} + (e_1 - e_2)^{\frac{1}{4}}} = \frac{(r + a)^{\frac{1}{2}} - |r - a|^{\frac{1}{2}}}{(r + a)^{\frac{1}{2}} + |r - a|^{\frac{1}{2}}},$$

then q can be computated from

$$q = \frac{l}{2} + 2\left(\frac{l}{2}\right)^5 + 15\left(\frac{l}{2}\right)^9 + 150\left(\frac{l}{2}\right)^{13} + O(l^{17}).$$

At a distance from the edge of the loaded circle, l is a fairly small quantity and consequently the terms after second or third may be dispensed with. The q series of the functions needed here are as follows:—

$$\eta_{1} + e_{1}\omega_{1} = \frac{\pi^{2}}{\omega_{1}} \left\{ \frac{1}{4} + 2 \sum_{n=1}^{\infty} \frac{q^{2n}}{(1 + q^{2n})^{2}} \right\},$$

$$\omega_{1} = \frac{\pi}{2} \left( \frac{\alpha}{2} \right)^{\frac{1}{2}} \vartheta_{2}^{2}(0),$$

$$\frac{1}{2} e_{1}\omega_{1} - \eta_{1} = \frac{1}{8\omega_{1}} \left\{ \frac{\vartheta'''_{1}(0)}{\vartheta'_{1}(0)} - \frac{\vartheta''_{2}(0)}{\vartheta_{2}(0)} \right\};$$

$$\vartheta_{2}(0) = 2q^{\frac{1}{4}} \left( 1 + q^{2} + q^{6} + q^{12} + \ldots \right),$$

$$\vartheta'''_{1}(0) = -2\pi^{3}q^{\frac{1}{4}} \left( 1 - 3^{3}q^{2} + 5^{3}q^{6} - 7^{3}q^{12} + \ldots \right),$$

$$\vartheta''_{1}(0) = 2\pi q^{\frac{1}{4}} \left( 1 - 3q^{2} + 5q^{6} - 7q^{12} + \ldots \right),$$

$$\vartheta''_{2}(0) = -2\pi^{2}q^{\frac{1}{4}} \left( 1 + 3^{2}q^{2} + 5^{2}q^{6} + 7^{2}q^{12} + \ldots \right).$$

At the point near the edge of the loaded circle, the above expansions cease to be applicable. For this case, our object will be accomplished by using the quantity  $q_1$ , instead of q, which is defined by

$$q_1 = e^{i\pi \tau_1}, \qquad \tau_1 = -\frac{\omega_1}{\omega_2} = -\frac{1}{\tau}.$$

 $q_1$  is calculated from

$$q_1 = \frac{l_1}{2} + 2\left(\frac{l_1}{2}\right)^5 + 15\left(\frac{l_1}{2}\right)^9 + 150\left(\frac{l_1}{2}\right)^{13} + O\left(l_1^{17}\right),$$

in which

$$l_1 = \frac{(e_1 - e_3)^{\frac{1}{4}} - (e_2 - e_3)^{\frac{1}{4}}}{(e_1 - e_3)^{\frac{1}{4}} + (e_2 - e_3)^{\frac{1}{4}}} = \frac{(r + a)^{\frac{1}{2}} - (2(ar)^{\frac{1}{2}})^{\frac{1}{2}}}{(r + a)^{\frac{1}{2}} + (2(ar)^{\frac{1}{2}})^{\frac{1}{2}}}.$$

For example, to calculate  $\left(\frac{\partial u_z}{\partial r}\right)_0$  near the edge, we proceed like this:—

By the aid of the relation

$$\frac{\mathcal{G}'''_{1}(0)}{\mathcal{G}'_{1}(0)} = \frac{\mathcal{G}''_{0}}{\mathcal{G}_{0}} + \frac{\mathcal{G}''_{2}}{\mathcal{G}_{2}} + \frac{\mathcal{G}''_{3}}{\mathcal{G}_{3}},$$

the function  $\frac{1}{2}e_1\omega_1-\eta_1$  may be transformed into

$$4\pi \left(\frac{\alpha}{2}\right)^{\frac{1}{3}} \left(\frac{1}{2}e_1\omega_1 - \eta_1\right) = \frac{1}{\vartheta_2^{-2}(0\mid \tau)} \left\{ \frac{\vartheta_0''(0\mid \tau)}{\vartheta_0(0\mid \tau)} + \frac{\vartheta_3''(0\mid \tau)}{\vartheta_3(0\mid \tau)} \right\} \cdot$$

Making use of the transformation formulæ of Theta-functions it will be easily shown that

$$\frac{\Im''_{0}(0|\tau)}{\Im_{0}(0|\tau)} = 2i\pi\tau_{1} + \tau_{1}^{2} \frac{\Im''_{2}(0|\tau_{1})}{\Im_{2}(0|\tau_{1})},$$

$$\frac{\vartheta''_{3}(0|\tau)}{\vartheta_{3}(0|\tau)} = 2i\pi\tau_{1} + \tau_{1}^{2} \frac{\vartheta''_{3}(0|\tau_{1})}{\vartheta_{3}(0|\tau_{1})}$$

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and

$$\vartheta_2^2(0|\tau) = -i\tau_1\vartheta_0^2(0|\tau_1),$$

consequently we have

$$\frac{1}{2}e_{1}\omega_{1} - \eta_{1} = \left(\frac{2}{\alpha}\right)^{\frac{1}{2}} \frac{4}{\vartheta_{0}^{2}\left(0 \mid \tau_{1}\right)} \left\{-4 + \frac{\log_{e} q_{1}}{\pi^{2}} \left[\frac{\vartheta''_{2}\left(0 \mid \tau_{1}\right)}{\vartheta_{2}\left(0 \mid \tau_{1}\right)} + \frac{\vartheta''_{3}\left(0 \mid \tau_{1}\right)}{\vartheta_{3}\left(0 \mid \tau_{1}\right)}\right]\right\}.$$

The  $q_1$  series for the functions required here are

$$\begin{split} &\beta_0 = 1 - 2q_1 + 2q_1^4 - 2q_1^9 + \dots, \\ &\beta''_2 = -2\pi^2 q_1^{\frac{1}{4}} \left( 1 + 3^2 q_1^2 + 5^2 q_1^6 + 7^2 q_1^{12} + \dots \right), \\ &\beta_2 = 2q_1^{\frac{1}{4}} \left( 1 + q_1^2 + q_1^6 + q_1^{12} + \dots \right), \\ &\beta''_3 = -8\pi^2 \left( q_1 + 4q_1^4 + 9q_1^9 + \dots \right), \\ &\beta_3 = 1 + 2q_1 + 2q_1^4 + 2q_1^9 + \dots. \end{split}$$

In the accompanying diagram the courses of  $(u_z)_0$  and its slope are exhibited as functions of the distance of the point of observation from the centre of the loaded

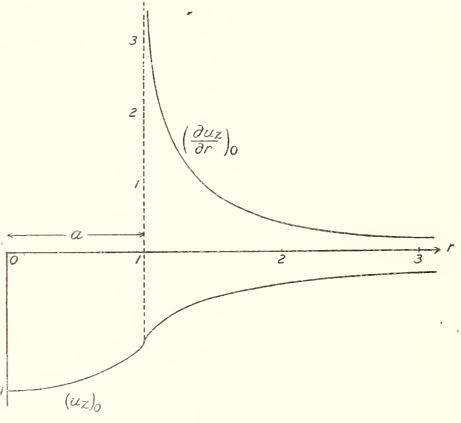


Fig. 1.

circle, with the proper scale. The lower curve thus represents the vertical displacement and the upper one the corresponding slope outside of the loaded area.

If we like North Atlantic to a circular basin of a large radius and determine the relative position of Potsdam or Chicago referred to the centre of it, the attraction effect and the tilting effect of the periodic filling and emptying of tide, which might assist in producing the extra east-west force, in observations of lunar disturbance of gravity, may be computed. If we suppose the place of the observation to be not very near to the circular basin, the effect, as we see from the above diagram, is of course small, but it increases rapidly as the edge is approached.

For example, suppose the radius of the North Atlantic basin to be 2000 km., the position of Chicago to be 3000 km. from the centre, and the level of the water in this area to be raised one meter, then

$$\frac{r}{a} = 1.5, \qquad q_1 = 0.00255,$$

and

$$a\alpha^2(\frac{1}{2}e_1\omega_1-\eta_1)=0.8639.$$

Further assume that the density of sea water is 1, and in c.g.s. units,

$$\gamma = 6.65 \times 10^{-8}, \qquad g = 980,$$

$$\frac{\lambda + 2\mu}{2(\lambda + \mu)} = \frac{3}{4}, \qquad \mu = 6 \times 10^{11},$$

then we shall have

$$\psi = 1.17 \times 10^{-8} = 0^{"}.0024,$$

$$\phi = 3.37 + 10^{-8} = 0$$
".0069.

Accordingly the total effect amounts to

$$\psi + \phi = 4.54 \times 10^{-8} = 0$$
".009.

It will be noticed that the effect of tilting is about three times as great as that of the attraction, so far as the material constants are assumed as above. According to Lord Kelvin,\* who initiated these investigations, the direct lunar effect on the deviation of a plumbline is a maximum when the moon is at the altitude 45 degrees and amounts to 0"'017 nearly. The total effect of a tide of amplitude one metre (which is possibly two or three times the actual amount) found here is not small enough to be neglected compared with the direct effect of the moon, the former is nearly half the latter. As the tilting effect and the attraction effect of the tide wave are directly proportional to the height of the tide, the total effect oscillates in time in accordance with the law which the tide obeys. There is, in general, a difference in phase between the lunar effect and the tidal effect, which is worthy of closer investigation.† But we must bear in mind that the calculation adopted here is nothing but a rough estimation of order of magnitude, since the North Atlantic is far from circular, the tidal loading in it is never uniform.

<sup>\* &#</sup>x27;Natural Philosophy,' Part II., p. 383.

<sup>†</sup> Fortunately, the phase difference of both effects in MICHELSON'S experiment may be neglected in a rough estimation, owing to the relative position of Chicago and the centre of the North Atlantic.

Nevertheless the above analysis shows that the tidal effect on the water-level measurement, even at a point as far from the coast as Chicago, plays an important rôle and cannot be regarded as a small correction.

## IV. Elliptic Loading.

Next, let us suppose that the tide in the North Atlantic is not uniform, but its surface is given by the equation

$$\frac{z^2}{b^2} + \frac{r^2}{a^2} = 1, \quad z < 0,$$

viz., the excess pressure on the bottom due to the tide diminishes on approaching the coast so as to amount to

$$\widehat{zz} = -\frac{bg\rho}{a} (a^2 - r^2)^{\frac{1}{2}} \quad \text{for} \quad r < a,$$

$$= 0 \qquad ,, \quad r > a.$$
(26)

In this case the function Z(k) becomes

$$Z(k) = -abg\rho \left\{ \frac{\sin ka - ka \cos ka}{k^2 a^2} \right\} . . . . . (27)$$

Therefore we have

$$u_{z} = \frac{abg\rho z}{2\mu} \int_{0}^{\infty} e^{-kz} \left\{ \frac{\sin ka - ka \cos ka}{k^{2}a^{2}} \right\} J_{0}(kr) dk$$
$$+ \frac{a^{2}bg\rho (\lambda + 2\mu)}{2\mu (\lambda + \mu)} \int_{0}^{\infty} e^{-kz} \left\{ \frac{\sin ka - ka \cos ka}{k^{3}a^{3}} \right\} J_{0}(kr) dk, \tag{28}$$

and

$$\left(\frac{\partial u_z}{\partial r}\right)_0 = -\frac{abg\rho\left(\lambda + 2\mu\right)}{2\mu\left(\lambda + \mu\right)} \left[\int_0^\infty e^{-kz} \left\{\frac{\sin ka - ka\cos ka}{k^2 a^2}\right\} J_1(kr) dk\right]_{z=0}.$$
(29)

The integrals contained in the above can be obtained by expanding the trigonometrical functions into power series of k and making use of the formula

$$\int_{0}^{\infty} e^{-kz} k^{n} J_{m}(kr) dk = \frac{(n-m)!}{(r^{2}+z^{2})^{\frac{n+1}{2}}} P_{n}^{m} \left(\frac{z}{\sqrt{(r^{2}+z^{2})}}\right).$$

Thus

$$u_{z} = \frac{abg\rho z}{\mu \left(r^{2} + z^{2}\right)^{\frac{1}{6}}} \sum_{n=1}^{\infty} (-1)^{n-1} \frac{n \left(2n-1\right)!}{(2n+1)!} \left(\frac{a}{\sqrt{(r^{2} + z^{2})}}\right)^{2n-1} P_{2n-1}(\nu)$$

$$+ \frac{a^{2}bg\rho \left(\lambda + 2\mu\right)}{\mu \left(\lambda + \mu\right) \left(r^{2} + z^{2}\right)^{\frac{1}{2}}} \sum_{n=1}^{\infty} (-1)^{n-1} \frac{n \left(2n-2\right)!}{(2n+1)!} \left(\frac{a}{\sqrt{(r^{2} + z^{2})}}\right)^{2n-2} P_{2n-2}(\nu), \quad (30)$$

where

$$\nu = \frac{z}{\sqrt{(r^2 + z^2)}}.$$

These series converge for  $\sqrt{(z^2+r^2)} > a$ , and are applicable in this region.

At the surface we have to put z = 0 and  $\nu = 0$ . Since

$$P_{2n-2}(0) = (-1)^{n-1} \frac{1 \cdot 3 \dots 2n-3}{2 \cdot 4 \dots 2n-2},$$

we have

$$\int_{0}^{\infty} \frac{\sin ka - ka \cos ka}{k^{3}a^{3}} J_{0}(kr) dk = \frac{1}{3r} F\left(\frac{1}{2}, \frac{1}{2}, \frac{5}{2}, \frac{a^{2}}{r^{2}}\right)$$

$$= \frac{1}{2a} \left\{ \left(1 - \frac{r^{2}}{2a^{2}}\right) \sin^{-1} \frac{a}{r} + \frac{r}{2a} \left(1 - \frac{a^{2}}{r^{2}}\right)^{\frac{1}{2}} \right\}. \quad (31)$$

Consequently

$$(u_z)_0 = \frac{abg\rho(\lambda + 2\mu)}{4\mu(\lambda + \mu)} \left\{ \left(1 - \frac{r^2}{2a^2}\right) \sin^{-1}\frac{a}{r} + \frac{r}{2a} \left(1 - \frac{a^2}{r^2}\right)^{\frac{1}{2}} \right\} . . (32)$$

for  $r \ge a$ .

To find the expression for the vertical displacement within the loaded circle we proceed as follows:—

Making use of the power series of Bessel's function, we have

$$\int_{0}^{\infty} e^{-kz} \left\{ \frac{\sin ka - ka \cos ka}{k^{3}a^{3}} \right\} J_{0}(kr) dk = \frac{1}{a} \sum_{n=0}^{\infty} \frac{(-1)^{n}}{(n!)^{2}} \left( \frac{r}{2a} \right)^{2n} \Omega_{2n} \left( \frac{z}{a} \right), \quad (33)$$

where  $\Omega$  stands for

$$\Omega_{m}(x) = \int_{0}^{x} e^{-\lambda x} \left\{ \frac{\sin \lambda - \lambda \cos \lambda}{\lambda^{3}} \right\} \lambda^{m} d\lambda.$$

The evaluation of the function  $\Omega_{m}(x)$  can be undertaken by the aid of the formulæ

$$\int_0^\infty e^{-\lambda x} \frac{\sin \lambda}{\lambda} d\lambda = \tan^{-1} \frac{1}{x},$$

$$\int_0^\infty e^{-\lambda x} \cos \lambda d\lambda = \frac{x}{1+x^2}.$$

A little calculation will give us

$$\Omega_0(x) = \frac{\pi}{4} - \frac{1}{2} \left\{ x + \tan^{-1} x - x^2 \tan^{-1} \frac{1}{x} \right\},$$

$$\Omega_1(x) = 1 - x \tan^{-1} \frac{1}{x},$$

$$\Omega_{2}(x) = \tan^{-1}\frac{1}{x} - \frac{x}{1+x^{2}},$$

$$\Omega_3(x) = \frac{2}{(1+x^2)^2},$$

and, in general,

$$\Omega_m(x) = (-1)^{m-1} \frac{d^{m-3}}{dx^{m-3}} \left(\frac{2}{(1+x^2)^2}\right) \quad m > 2.$$

Thus the integral on the left-hand side of (33) can be expanded in an ascending power series of r/a which probably converges for limited values of r if the value of z is fixed. This series and that found in (30) have a common region in which they are both convergent and therefore they must be congruent to each other in that region. On the proof of this proposition we shall not enter, but we shall find the region of convergency of the latter series at the boundary.

Expand  $\Omega_{2n}\left(\frac{z}{a}\right)$  into a power series of z/a, supposing z/a to be sufficiently small, then the first term of it will be  $(-1)^n 2(n-1)(2n-2)! \frac{z}{a}$ . If we retain only the terms which contain the first power of z/a in the series of (33), its general term will then be

$$\frac{2(n-1)(2n-2)!}{(n!)^2 2^{2n}} \left(\frac{r}{a}\right)^{2n} \cdot \frac{z}{a}.$$

The series which has this expression as its general term converges obviously for the values of r smaller than a. Thus the expansion (33) applies for r < a when z is an infinitesimal.

Since, for z = 0,

$$\Omega_{0}(0) = \frac{\pi}{4}, \quad \Omega_{2}(0) = \frac{\pi}{2}, \quad \Omega_{4}(0) = 0, \quad \Omega_{6}(0) = 0, \quad \dots,$$

we have

$$\int_{0}^{\infty} \frac{\sin ka - ka \cos ka}{k^{3}a^{3}} J_{0}(kr) dk = \frac{\pi}{4a} \left\{ 1 - \frac{1}{2} \left( \frac{r}{a} \right)^{2} \right\}, \quad (34)$$

for  $r \leq a$ .

Hence

$$(u_z)_0 = \frac{\pi a b g \rho \left(\lambda + 2\mu\right)}{8\mu \left(\lambda + \mu\right)} \left\{ 1 - \frac{1}{2} \left(\frac{r}{a}\right)^2 \right\}, \quad . \quad . \quad . \quad . \quad (35)$$

for  $r \leq a$ .

Quite similar arguments may be employed to find the expression for the tilting. We shall have

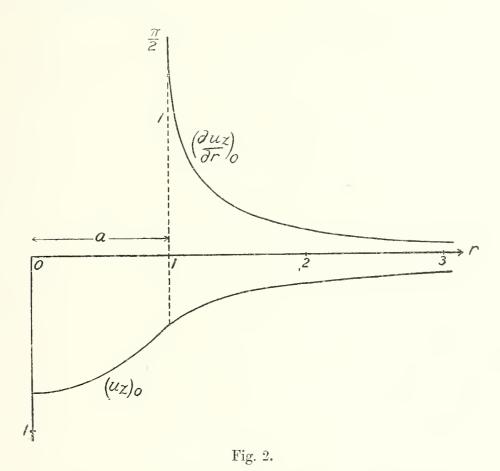
$$\int_{0}^{\infty} \frac{\sin ka - ka \cos ka}{k^{2}a^{2}} J_{1}(kr) dk = \frac{r}{2a^{2}} \left\{ \sin^{-1}\frac{a}{r} - \frac{a}{r} \left( 1 - \frac{a^{2}}{r^{2}} \right)^{\frac{1}{2}} \right\}, \quad r \ge a, \\
= \frac{\pi r}{4a^{2}}, \qquad r \le a. \tag{36}$$

Consequently

$$\left(\frac{\partial u_z}{\partial r}\right)_0 = -\frac{bg\rho\left(\lambda + 2\mu\right)}{4\mu\left(\lambda + \mu\right)} \cdot \frac{r}{a} \left\{ \sin^{-1}\frac{a}{r} - \frac{a}{r} \left(1 - \frac{a^2}{r^2}\right)^{\frac{1}{2}} \right\}, \quad . \quad . \quad (37)$$

for  $r \ge a$ .

The general march of the function  $(u_z)_0$  and  $\left(\frac{\partial u_z}{\partial r}\right)_0$  are shown in the attached diagram (fig. 2) in a suitable scale. The lower curve represents the vertical displacement and the upper one the slope of the ground. The course of the curves is very similar to that of fig. 1, as we would expect, except at the points very near to the edge of the loaded area, where, as there is no discontinuity in the load in this case, the slope remains finite.



Let us take an example, with the same assumption regarding the various constants and the position of the point of observation as in the former example, and suppose that the total amount of the load is the same as before, *i.e.*, the mean height of the tide is one metre. Then we shall have

$$\psi = 1.12 \times 10^{-8} = 0''.0023,$$

$$\phi = 3.21 \times 10^{-8} = 0''.0066,$$

$$\psi + \phi = 4.33 \times 10^{-8} = 0''.009,$$

and

nearly the same as the result in the former example.

If we suppose the place of the observation to be nearly at the edge of the loaded area, then

$$\psi = 5.0 \times 10^{-8} = 0^{".01},$$

$$\phi = 14.4 + 10^{-8} = 0^{\prime\prime}.03,$$

and

$$\psi + \phi = 0^{\prime\prime}.04,$$

amounting to more than the direct lunar effect itself, notwithstanding that the load falls off towards the coast.

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[PLATE 1.]



# THE GENESIS OF PLEOCHROIC HALOES.



BY

J. JOLY, Sc.D., F.R.S.,
PROFESSOR OF GEOLOGY AND MINERALOGY IN THE UNIVERSITY OF DUBLIN.

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### III. The Genesis of Pleochroic Hatoes.

By J. Joly, Sc.D., F.R.S., Professor of Geology and Mineralogy in the University of Dublin.

(Received June 1,—Read June 29, 1916.)

[Plate 1.]

### Introduction.

In an earlier paper on the subject of pleochroic haloes\* it was pointed out that several features of the halo derived from the uranium family of radioactive elements were not easily accounted for. This fact led me to undertake a more careful study of haloes. But, although many observations and measurements were made, until recently my attempts at obtaining solution of the difficulties were too crude to merit publication. They were more especially hampered by the scarcity of haloes derived from the thorium family of elements. I could find out nothing as to the mode of origin of these haloes, and, on the observations available, it even appeared as if there were some unaccountable difference in the course of development of the haloes derived from the uranium and the thorium families. The initial stages of development seemed to be entirely absent in the case of the thorium series. This was not satisfactory. A few months ago, however, I found in a Vosges granite, a mica which was rich in thorium haloes. Some of these haloes appeared in the earlier stages of development; stages corresponding to the earliest in the development of the uranium This find showed that the same course was followed in the genesis of both kinds of halo.

The find was also important in another respect. Certain small discrepancies between the observed and the theoretic dimensions of the uranium halo had been forced on me as the measurements became more refined. This, of course, led me to distrust the basis upon which I was going in attempting to define theoretic dimensions. But in the developing thorium halo it would appear as if the basis of my predictions was uniformly supported. This seems to show that there is something anomalous, according to our existing knowledge of the ranges, in the early development of the uranium halo.

There was another difficulty which I have only lately been able to clear away. There were found to exist in the Leinster granite of County Carlow a very large number of embryonic haloes having dimensions uniformly and distinctly greater than those which I had been led to regard as the initial form of the uranium halo. And these larger haloes showed not the least trace of the existence of the lesser

haloes, although plainly representing an early stage of the uranium halo. Here again it appeared as if some unknown factor existed which could occasion different modes of origin for a halo. However, the idea that the larger embryos might be traceable to radium emanation acting as the parent element was found to afford a quite adequate explanation of the phenomenon. Additional evidence for this view is found in the fact that these haloes are almost invariably found located on conduits or veins in the mica; conduits which undoubtedly conveyed radioactive materials at And even when we cannot demonstrate the existence of such a some past time. conduit we find in the linear arrangement of these haloes evidence that they have been generated along a crack or vein. The nature of the nucleus of these interesting haloes is not determinable. It is probably zircon. Whatever the mineral substance is, we must ascribe to it the power of absorbing or occluding the emanation and so becoming a centre of radiation of the α-rays of emanation and of the derived series of elements.

I cannot claim to have been able to suggest explanations of every difficulty. Quite the contrary; with increased number of observations fresh questions present themselves. These appear, so far, to be confined to the behaviour of the less penetrating  $\alpha$ -rays of the uranium series of elements.

I have included in this paper an attempt at an explanation of the reason why the halo develops as it does. It is not hard to show that  $prim\hat{a}$  facie the structural features of haloes are not what one would expect on theoretical grounds. By introducing the assumption that haloes partake of the properties of the latent photographic image and are capable of "reversal" or "solarisation" under certain conditions, it seems to be possible to explain the observed structural features. Quite lately I have found that a phenomenon is sometimes apparent in haloes which appears to set the possibility of solarisation or reversal beyond doubt. I have added a drawing of a reversed halo.

### Method of Measurement.

From time to time considerable modifications have been introduced into the methods of effecting the measurement of haloes. The earlier observations were generally made with too low a magnification. There were also other causes of uncertainty. Much of the variation among the measurements disappeared under improved conditions of observation. But with all improvements the readings require care and practice. A Leitz micrometer eyepiece and a Leitz No. 4 objective give about the best magnification and conditions for reliable measurements. But the mode of using the micrometer is important. The usual practice in such cases is to traverse the image with the moving line of the micrometer, reading the micrometer head when the line is in diametrically extreme positions on the image. This method is defective for two reasons. It is difficult to secure any degree of accurate setting of the line when this is leaving the image. To

avoid back-lash, we must move the micrometer head always in the one direction. The adjustment cannot, therefore, be made by tentative movements, and, in consequence, it is likely to be erroneous. Again, we have to remove the eye for the first reading. Hence, if there is parallax error, we may come in for it. The following method has been found much better: The image of the halo is brought into tangential contact with one of the fine fixed lines of the eyepiece. This is effected to a nicety by placing the halo a little excentrically in the field and rotating the stage of the microscope. Next, the travelling wire is brought into tangential contact with the other limb of the halo. This adjustment is effected by successive trials, always withdrawing the line, and again bringing it up against the halo. Finally, leaving the micrometer at this setting, we investigate the fit of the halo between the lines by rotating back and forward the stage of the microscope. We also investigate the effects of slight changes in the focus. If all is satisfactory, we lastly read the amount of rotation of the head which is requisite, in order to bring the two lines into juxtaposition. Superimposition of the lines will read some constant even number determined in the setting of the head. But when the measured diameter of a nucleus has to be deducted—as is generally the case—the correction for the width of the line is automatically made if the readings for superimposition are adhered to throughout.

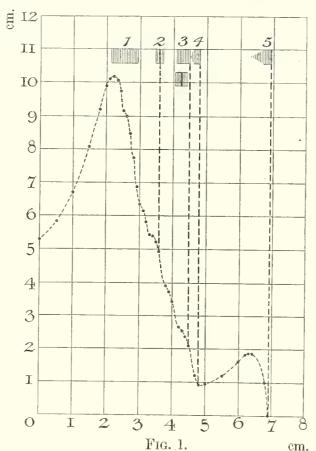
In general, the chief difficulty is in placing the lines truly tangential to the halo-image. The difficulty increases with the faintness of the halo, and the faint early haloes are those of most interest, as will presently be seen. But with good lighting, and after shading the eye for some time, very consistent readings can be obtained. The doubtfulness of the readings does not amount in favourable cases to as much as two divisions of the micrometer head. Now, with the optical conditions referred to above, 113 divisions of the head correspond to a travel of the line of 0.05 mm. in the field of the microscope. One division, therefore, corresponds to 0.0044 mm. in the field. Hence those smaller haloes, which read about 0.022 mm. in diameter, should be measured upon each reading to an accuracy of about 4 per cent. One point I would specially call attention to: the advantage attending the use of the rotating stage of the microscope when testing the adjustment of the lines upon the image. This is greatly due to the increased sensitiveness of vision obtained by the mere movement of the image. It is doubtless a question of transferring the image to an unfatigued part of the retina. I have long been familiar with this phenomenon, and I believe it is known to many microscopists.

## Theoretical Views as to the Formation of Haloes.

The halo is the result of the ionising effects of the  $\alpha$ -rays proceeding from the central nucleus. By a fundamental law of radioactivity, an equal number of  $\alpha$ -rays is emitted by each contributory element. We assume that the nucleus is small in

radius compared with the ranges of the rays concerned. In this case the several rays move along the radii of a sphere having the nucleus at its centre. They therefore diverge like rays of light from a luminous point, and the intensities, or more accurately the closeness of approximation, of the effects, upon successive spherical surfaces, must diminish outwards with the inverse square of the distance. But this inverse square law is departed from in the particular that the effect of any one ray is not in itself a uniform one along its path. The observations of Bragg and others have shown that, just before the electrified particle loses its kinetic energy, there is a rapid increase in its power of ionisation. A limit to this increase is attained some little time before the power of ionisation ceases. The curve depicting these facts is well known. Its definition, as determined by Geiger,\* is used in the applications of it which I make in what follows.

We seem, then, entitled to expect that a halo would show features in general accordance with the following scheme of development. We first assume that the medium possesses the stopping power and other properties of air. Along a horizontal axis we then repeat the Geiger curve for each constituent  $\alpha$ -ray concerned in



generating the halo, placing the outer termination of the curve accurately according to the range of each ray. At sufficiently close points along the horizontal axis we then add the ordinates of the overlapping curves. The summation of these ordinates gives us such a curve of ionisation as would correspond to the action of a parallel sheaf of rays. Brage obtained observationally such a curve in the case of radium and its derived elements.

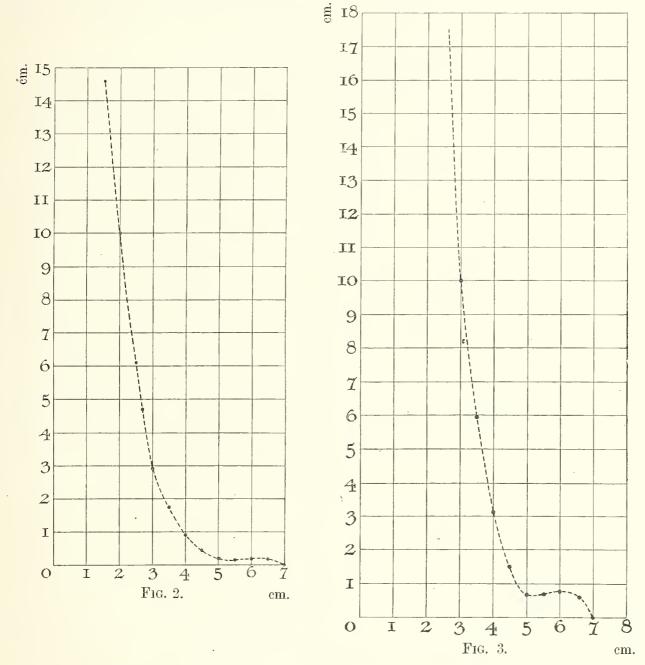
But this curve does not take into account the spreading of the rays which, from our knowledge of the spherical form of the halo, is a mere geometrical necessity, and cannot be evaded. When, now, we divide the successive integral ionisation ordinates by the square of their abscisse, we obtain a curve which should, according to the assumptions already made, define the gradation of density outwards from the centre of the halo. Rock sections of

ordinary thickness, and cleavage flakes of mica, include only a part of the halo sphere—perhaps one-third or one-fourth of it—and this will modify the appearance a little.

I give here the results of these successive operations. Fig. 1 is the result of an accurate summation of the ordinates of the Geiger curve, placed according to the

\* 'Roy. Soc. Proc.,' A, vol. 82, p. 486 (1909).

ranges of the eight rays of the uranium family, as cited in RUTHERFORD'S 'Radioactive Substances and their Transformations.' The curve is put in according to a carefully made template. The added ordinates are reduced to one-fourth their full length. Fig. 2 shows the result of dividing the ordinates by the squares of the abscissæ. Fig. 3 is, finally, the latter curve corrected for perspective in the case



when the observed halo is a section symmetrical about the centre and 4 cm. thick—i.e., about one-third the diameter of the halo sphere.\*

<sup>\*</sup> This last correction is a troublesome one. We assume the halo sphere divided into concentric shells, each, say, one half a centimetre thick, measured radially. To each of these shells we assign an intensity of ionisation, as defined by the ordinate of the curve of fig. 2, taken at the centre of the half centimetre. Drawing these concentric shells on squared paper, and defining by cross lines the upper and lower boundary of the section, we can evaluate, at successive distances of one half centimetre from the centre, the intensity of ionisation which would operate to darken the halo when this is observed by vertical rays proceeding from beneath.

Now, according to figs. 2 and 3, the halo should appear with a much darkened central disc or pupil, this disc being surrounded by a relatively very faint band or penumbra-like shading. For we see that the spreading of the rays, according to the inverse square law, has much reduced the maximum due to RaC. I am supposing now that we can translate the effects in air into effects in the mineral by simply shortening the ranges by the amounts proper to the greater stopping power of the mineral. That is, I assume that the curve defining the ionisation in air is followed in its general features in the mineral.

Many haloes may indeed appear to conform fairly well with the distribution of ionisation shown in figs. 2 and 3. Photographs issued elsewhere show such haloes.\* But, in point of fact, when we come to examine the halo in its earlier stages of development we find the appearance indicated by figs. 2 and 3 (ante) entirely departed from. Published photographs show that in its earlier stages the halo consists of concentric rings—or, more strictly, of shells—of varying density of colour.†

In many respects we find that the curve fig. 1 very faithfully represents the development of the uranium halo. In the first stages we have a delicate ring which is clearly representative of, although not accurately agreeing with, the remarkable maximum which is placed at the distance in air of 2.2 cm. from the centre or origin. Later we find this ring darkened up inside, and the first appearances of RaC presented as a faint outlying ring. But here there is plainly a discordance. The appearance of the shell due to RaC should be delayed till a much later stage in the development of the halo. Plainly, according to the ionisation curve, the central pupil should be carried out in air to a distance of about 4.5 cm. before the first indications of the outermost band appear. In the development of the region lying between the minimum of ionisation (at 4.8 cm.) and the embryonic ring two distinct shells may be detected.

These facts of observation show that the uranium halo develops very much as if the inverse square law did not operate at all or acted but partially, and it is evident that the final state of a halo according to fig. I is quite in accordance with the photographs referred to above. In a word, the development of the halo, as observed, indicates that for some reason the divergence of the rays which should lead to the obliteration of the features of the ionisation curve of fig. I, is counteracted, and the maxima of the several rays, which contribute to the formation of the curve, sustained. I may add here that in the case of the development of the thorium halo the adherence of its genesis to the curve of ionisation derived from the integration of parallel rays is even more striking.

I suggest the following explanation, although in itself invoking the aid of very obscure phenomena. It is known that the first effects of stimuli applied to the photographic plate are reversible by other stimuli. Wood has shown that these

<sup>\* &#</sup>x27;Phil. Mag.,' loc. cit., Plate 8; 'Proc. R. Dublin Soc.,' XIII, Plate 3, figs. 2 and 3.

<sup>† &#</sup>x27;Proc. R. Dublin Soc.,' loc. cit., figs. 5 and 6.

stimuli will only reverse one another's effects if applied in a certain order. Thus the latent image due to friction or pressure is obliterated by any other known form of stimulus such as X-rays or light. Next in order of stability is the latent image due to X-rays. Light action will remove this. A very brief light shock or flash comes next. This can only be reversed by a long continued light stimulus. In this list the stimulus which produces the less stable system is unable to reverse the more stable It does not appear improbable that in the mineral the effects of the α-ray may correspond in character to photographic latent effects, that is, to effects of an incomplete character, no definite molecular rearrangement being accomplished as the result of ionisation and liberation of  $\delta$ -particles. There is not wanting independent evidence that this is what actually happens. It is known that the halo can be obliterated by heating the mica. This fact led the earlier observers into the curious notion that the halo was an "organic" effect. Presumably the idea was that it was a coloration due to carbon which became oxidised upon heat being applied. If the halo was due to the formation of a stable oxide of iron it seems certain that even a red heat would not affect it. And it is said that some haloes—very strongly developed ones—refuse to be dissipated by heat. Here we have what I think may be described as a reversing effect due to heat. Again the halo shows by its optical behaviour that it is in crystallographic continuity with the rest of the mica. has apparently been some intermolecular disturbance or strain set up by the ionising actions generating the halo, so that the light absorption towards a polarised ray is increased. But it continues to exhibit the optical properties of the original medium, and, presumably, retains much of the original structure. I shall assume that just as it can be reversed by intense heat so the coloration of the halo may be obliterated or reversed by other stimuli when these are of a certain kind, or that it may be so reversed at some stages of its genesis.

The effects going on in the part of the mica traversed by the rays are highly complex. The character of the ionisation due to each single  $\alpha$ -ray, as shown by the Bragg curve, suggests that at points along its path the ionising stimulus may be regarded as varying with the velocity of the ray. And we see that every part of the field around the nucleus, except the outermost region which is traversed by the rays of RaC or ThC<sub>2</sub> only, is exposed to the passage of rays of very varying speeds.

I assume that, within certain limits of distance and intensity, some of these stimuli are able to reverse the effects of prior stimuli. The successive effects may be separated by any time interval, but the space interval is limited, although dimensions considerably greater than molecular are involved. Moreover, there must be a certain order maintained in the succession of stimuli of different velocity just as in Wood's experiments.

The chance of a ray passing within a certain effective distance from any point at the radial distance r from the centre is, say,  $p/r^2$ . For two rays to pass within this

<sup>\*</sup> Wood, 'Phil. Mag.' [6], pp. 577-587 (1903).

same distance the chance is  $p^2/r^4$ . Hence the reversing effect falls off outwards, ceteris paribus, with the fourth power of the radius. But the weakening effect of the geometric conditions falls off as the square of the radius. If we could suppose the effects limited to these two only, we appear to possess a mechanism whereby the geometric law is disposed of, for the rate of diminution of the reversing effect outwards is such as must occasion an accumulation of effects per unit volume in the outer shells of the halo even greater than what takes place within.

If we supposed that the effect, say, of the slowest moving ray, at any particular distance from the centre, was exposed to reversal by all the faster moving rays which might pass within effective distance thereto, we can evidently account for an additional diminution of destructive effects outwards, for the several rays fall out one by one as the radius increases. It is in this way I would account for the early appearance of the effects of RaC or of ThC<sub>2</sub>; for of all the rays which go to build the halo, these alone are unaffected by such reversal effects; and, where overlap with other rays ceases, succeeding stimuli possess the same, or nearly the same, velocity. The geometric law indeed affects and must affect the growth of density in this part of the halo as in all other parts, but here alone it is the chief or only source of diminished density.

From this it will be seen that the complication of the effects responsible for the halo is probably very great. The possibilities are not exhausted with what has already been stated. But although exact treatment of the subject appears impracticable, I think it is probable that the solution of the difficulties is to be found somewhat on the lines indicated.

I have not been able to arrive at any alternative explanation on the basis of modifying the form of the Bragg or Geiger curve. However much, within reason, we accentuate the final effects of the ray, the geometric law of spreading destroys the accentuation of those features of the integral ionisation curve which plainly account for the structure of the halo. Moreover, it is evident that no modification of the elementary ionisation curve can account for the early prominence of the outer ring; for whatever modification we apply to the ionisation curve for a single ray must affect all the constituent rays alike, and hence all features of the integral curve rise and fall together.

It might appear that by studying the effects obtaining in the mica where two haloes overlap, we might get evidence as to the existence of reversal effects. Unfortunately these effects seem very variable. Sometimes there is overlap with little or no increased depth of colour. This is favourable to the reversal theory. But, again, and when we have reason to believe that there is true overlap in the same plane, there is increase of darkening.

Since the above was written, I have found what seems to be a "reversed" halo. I give a drawing (Plate 1, fig. 5) shaded as nearly as I can judge similarly to the original. The dark outer band is due to RaC and has not been reversed. From its

width and depth of colour we infer that the halo, before reversal, was evidently much blackened. The entire central region has been more or less reversed. The narrow ring or shell which is almost the only internal feature left may be either a survival or a feature due to fresh ionisation.

I have, on rare occasions, previously found haloes having a similar appearance to this reversed halo; but their true significance was not appreciated by me. Whether they represent reversal as the result of the different stimuli successively acting, or as the result of over-exposure or "solarisation," it is impossible to say. But in either case they support the view that the halo partakes of the character of the latent photographic image.

### Effect of the Nucleus.

The nucleus is not a mathematical point. Its dimensions must play some part in contributing to the radial dimensions of the halo, and, consequently, in disguising the true range of the rays.

Exact evaluation of the nuclear effect is difficult or impracticable. Its effect probably varies with the stage of growth attained by the halo. Fortunately, in haloes such as enter into our present considerations, the nuclear effect is in any case small, and if the correction applied is not quite adequate, the remaining error must, of course, be still smaller.

We must consider the nucleus as composed of some substance possessing a stopping power differing from that of the mica. This applies to nuclei composed of zircon or uraninite, and to many other possible minerals. Zircon is the most probable of all. Within a zircon nucleus there will be a certain retardation of the ray in excess of what occurs for a similar travel in mica. Thus, availing ourselves of Bragg's Law, we may calculate that, in the mica (haughtonite) of Co. Carlow, a range of 1 cm. in air of density 0.0012 is represented by 0.0000473 cm. In this calculation the quotient a/d enters, where a is the average square root of the atomic weight of the retarding substance, and d is its density. Now for haughtonite the quotient has the value 1.6; for uraninite it is 1, and for zircon it is 1.1. The range is therefore less in zircon than in haughtonite as 1.1:1.6. We may take it as 2:3.

If we assume the rays to proceed from all points of the nucleus it is easy to show that the halo should exhibit, at least in its period of development, a border possessing a width about three times the radial dimensions of the nucleus, and shaded off both in its inner and outer margins. This border would exhibit a maximum depth of colour somewhere outside its mean radius, and if we measured the halo to this circle of maximum effect we should subtract one-third the radius of the nucleus in order to get the true range. In this reasoning the nucleus is supposed to be small compared with the size of the halo and sensibly spherical. Or we might expect at a later stage that the band would be darkened uniformly. If we then find the mean radius of this band the correction on this in order to determine the true range will be half the nuclear radius.

But in point of fact such borders have not been definitely identified. The sharp definition of the outer margin sometimes shown by a well darkened halo may be referable to such an effect of the nucleus. But the radius of the nucleus, in such haloes as are of importance to us, amounts to only 3 to 5 per cent. of the halo-radius. It seems more practical, therefore, to consider generally how much of this 3 or 5 per cent. might be deducted in order to obtain the true halo-radius or range which we seek to measure. Now we may take it that in developing haloes those radioactive particles which are placed on the outer surface of the nucleus will not sensibly affect the mica and we must make some assumption as to the depth in the nucleus from which those rays proceed which give us a visible effect, that is, which define that part of the boundary of the halo to which we bring the lines of the micrometer. I take this depth as one-third the radius inward from the surface of the nucleus. If not quite accurate this assumption must at least reduce such error as must arise if we neglect the effects of the nucleus altogether.

On this assumption, and further assuming that the stopping power of the nucleus is that of zircon, we have the effective defining ray advanced from the centre of the nucleus by  $\frac{2}{3}r$  (the nuclear radius) and again brought back, as it were, by the greater retardation experienced in traversing the distance r/3 in zircon. The loss of range due to the latter effect is r/6. Hence the net displacement outwards is r/2. Generally throughout this paper I have adopted this correction. I have not in all cases tabulated the nuclear measurements, for they are very uniform.

The correction in the case of the emanation halo may require different treatment. In this case there is some reason to believe that the radioactive substances giving rise to the halo may have been occluded on the surface of the nucleus or had penetrated but a short distance inwards. In such a case the correction for the nuclear radius must be the full amount of this radius. This is the correction I have applied in the case of emanation haloes. I have tabulated the nuclear radius of these haloes, however, as they are somewhat abnormally large. Besides it is possible to urge reasons for a different treatment of the nuclear correction.

### The Uranium Halo.

The first beginning of the uranium halo is a delicate shell surrounding the nucleus and possessing an external radius which has been measured from 0.013 to 0.015 mm. The measurements given below have been made with much care. The nuclei in the case of these embryonic haloes are generally very small and in many cases exceedingly small. They may appear as minute black points in the centre of the band-like ring which constitutes the halo as seen in section. The black speck is sometimes larger than the nucleus, which with a high power may be made out as a refracting particle within it. The internal radius of the ring is lettered  $r_1$  and the external radius r. I call this halo the first ring.

It would be easy to cite many other readings in good agreement with these.

Nos. 4, 5, and 6 are readings on three haloes which Prof. H. H. Dixon, F.R.S., was so good as to make. These measurements were obtained without any possibility of preconceived ideas influencing the judgment one way or the other. My own independent readings on these same haloes same in the mean to exactly the same figure arrived at by Prof. Dixon. Nos. 12 and 13 are measurements made by Mr. L. B. SMYTH, Lecturer in Palæontology in the School of Geology. These readings were obtained under the same conditions as obtained in the case of Prof. Dixon's measurements.

Table I.—Uranium Haloes: the First Ring.

	$r_1$ .	7.	Nuclear radius.
1	0.0112	0.0134	0.0004
$\frac{2}{3}$	0.0101	0.0149	0.0004
3	0.0099	0.0149	0.0002
	0.0098	0.0142	0.0006
5	0.0109	0.0153	0.0006
6	0.0106	0.0150	0.0006
4 5 6 7 8 9	0.0100	0.0139	0.0006
8	0.0101	0.0142	0.0006
9	0.0102	0.0145	0.0007
10	0.0106	0.0142	0.0006
11	0.0101	0.0139	0.0002
12	0.0100	0.0143	0.0006
13	States Prints	0.0140	
14	0.0107	0.0131	0.0003
15	0.0113	0.0137	0.0008
16	0.0110	0.0146	0.0010
17	0.0111	0.0142	0.0008
18	0.0113	0.0142	0.0008
	0.0102	0.0142	0.0006

No feature whatever is found within these rings, save in the more advanced stages, when a uniform darkening of the region between the ring and the nucleus appears. Many of the haloes cited above show no trace of this darkening. These are in the earliest measurable stage. It is possible to glimpse haloes surrounding nuclei still more point-like but which are too indefinite to permit of satisfactory measurement. But there is no reason to ascribe to them dimensions different to those recorded above.

Careful estimation, using a Leitz No. 5 objective, showed as the mean of seven observations that the width of the ring was to its outer radial dimension as 6·1:20·7. This determination was made on a medium dark halo; that is on one showing some darkening within the initiating ring. The same observation applied to a very faint ring gave the ratio as 5:19. There was less certainty here and it was found that the result might actually be 6:18. Using a lower power—a Leitz No. 3—another faint ring gave 37:27 as the ratio of the external to the internal diameter. This is nearly the same as the result 5:19 for ratio of width of ring to radius. Another

attempt applied to this last faint halo, using a Leitz No. 4, gave 24:70 as the ratio of width of band to radius. This nearly agrees with 6:18 as above. The external radius of this halo was measured as 0.0151, and the internal radius as 0.0104. These dimensions are subject to a small correction for the nucleus, which would leave the final readings as closely 0.0147 and 0.0100; and the mean radius becomes 0.0123. In the same flake of Carlow mica and near the last halo a sharp but faintly coloured ring was investigated in the same manner; the results were almost identical. Referring to the Table above we get  $(r-r_1)/r = 5/19$  nearly. The tabulated mean radius is 0.01235.

These minute haloes abound in the Carlow mica. In fact in places the clear mica is dusted over, as it were, with the black nuclear specks around which these haloes are formed, the delicate rings interlacing and overlapping in actual confusion. Some are, as already stated, so faint as to be hardly detectable. Others are well defined discs, the earliest formed part of the halo appearing as a darker border to the disc. One or two such growths are seen in the photographs already referred to. A vain endeavour was made to photograph the finer haloes but although many exposures and various combinations of lenses were tried nothing of value was obtained. The drawing (Plate 1, fig. 1) to a magnification of 800 is as realistic as I can make it.

A small correction has to be applied to these haloes for the effect of the nucleus in enlarging the radius. I have taken this as amounting to one-half the radius of the nucleus. This correction has been applied to the figures tabulated for  $r_1$  and r. The estimated radius of the nucleus is given in the fourth column.

These haloes are only well formed around very minute nuclei. Traces of them appearing round larger nuclei are not of value; the nuclear correction becomes too large and uncertain.

These haloes obviously correspond to the remarkable maximum of the curve of ionisation given, ante, fig. 1. They, therefore, must involve pre-eminently the ranges of  $U_1$  and  $U_2$ . But they do not possess the quite correct radius called for by the curve. Converting the range in mica into corresponding ranges in air the first ring is found to be placed in the position shown above the curve. The darkened area (marked 1) is a section of the ring halo.

A discussion of this point cannot be entered on till further facts are considered.

When the darkening within the first ring is yet only in its initial stages the outer shell due to RaC may begin to appear. This is seen in the published photographs.\* The extreme radius of the outer ring at this stage is very little less than it finally becomes. Attention has already been called to the bearing of the early appearance of the effects of RaC upon views as to the mode of origin of the halo.

Looking at the drawing, fig. 2, Plate 1, the first ring is seen almost lost in the darkening of the central region. This region has now become a "pupil." Around it in the form of a delicate ring appears the "second ring." The second ring is rarely seen. I have found it but twice in the Ballyellen mica, although some scores of haloes

<sup>\* &#</sup>x27;Proc. R. Dublin Soc.,' loc. cit., figs. 5 and 6.

sectioned in every plane must have been examined. I have found it twice in the Cornish granite. It would appear therefore to be more common in this granite, as of the number of haloes examined this is a much larger proportion. Finally, I recently found it in the Vosges granite.

In the case of the Ballyellen mica it was got by making serial sections of a halorich crystal of haughtonite. The object in view at the time was to test the sphericity of the halo by examination of successive sections. Two of the sections passing near and through the centres of two overlapping haloes showed the hitherto undiscovered ring, beautifully developed. In the drawing I have endeavoured to sketch one of these haloes to a scale of 800 diameters.

It will be seen that the new ring stands out specially dark and distinct. Its radial dimension has been the subject of many measurements. It has been read from 0.0172 to 0.0177 mm. But the result given for the two Ballyellen haloes, 0.0172, is for this mica very reliable. It appears to be referable to the prominence on the ionisation curve at the distance in air of 3.5 cm. from the centre.

In other features there is nothing abnormal about these complex haloes. The appearance of  $r_3$  is, however, an early one. They present a beautiful appearance. I give now the dimensions of the two Ballyellen haloes. The readings obtained were so much alike that it was found impossible to distinguish between them. The Vosges halo is a very thin section. The nucleus has left so indefinite a trace that it is difficult to be sure of the correction for it. I have taken a probable estimate.

R.  $r_1$ . 12. 13. Internal. External. Axis. External. Axis. External. Internal. External. (1) (2)0.0113 0.01500.01720.01880.02030.02170.02870.03270.01470.01720.01850.02050.02210.0327

Table II.—Uranium Haloes showing the Second Ring.

Nucleus of (1) and (2) 0.0009 mm. radius; q.p.

No. (1) is from Ballyellen, and (2) is from the Vosges granite. In the case of  $r_1$  and R the external and internal radii are given. In the case of  $r_2$  and  $r_3$  the external and axial radii of the ring are recorded. The nuclear correction has been applied.

It is not easy to account for the comparative rarity of these haloes. The second ring is, in all cases examined, accentuated in depth of colour. It is therefore not likely to escape notice.

The outward expansion and darkening of the central region of the halo follows and is found in every stage. This is in keeping with the development of the halo under the rapidly declining ionisation ordinates characterising the shape of the curve

outside the point of maximum ionisation. When this outward growth has considerably developed and the region of the second ring is darkened up a sharp and narrow ring appears encircling the enlarged pupil. The photographs reproduced in the 'Phil. Mag.,' and 'Proc. R. Dublin Soc.,' loc. cit., show this ring. The drawing, Plate 1, fig. 3, is from accurate measurements. Looking at the ionisation curve, fig. 1, we see only one feature which we can connect with it, the shoulder or prominence which is largely due to RaA where the ionisation of this ray is a maximum. I call this the third ring. The following Table gives some careful readings of the dimensions of the third ring and of the pupil which lies within it. The outside radius of the third ring is  $r_3$ ; its internal radius is r. The outside radius of the fourth ring is R:—

					Pupil.	r.	<i>7</i> °3.	R.
1	Carlow ha	ughtonite			0.0205	pate-rates	0.0227	0.0327
2	,,	,,			0.0207	****	0.0226	0.0327
3	,,	••			0.0202		0.0228	0.0330
4	11	11			0.0185	0.0196	0.0221	0.0329
5	44	, ,			0.0181	patenting	0.0189	0.0325
6	• • •	* ,			0.0185	patenting	0.0193	0.0325
7	Vosges				0.0185		0.0228	0.0331
		*			0.0193		0.0216	0.0328

Table III.—Haloes showing the Third Ring.

These results represent the normal type of halo showing the third ring. The average correction for nucleus is from 0.0004 to 0.0006. The degree of general darkening in the above cited haloes is very various. No. 4 is much the darkest.

Outside the third ring an annulus which very often is of quite unaltered mica appears. This evidently corresponds to the minimum of ionisation which begins at a distance of about 4.8 cm. from the origin of the curve, fig. 1. This annulus may be delicately shaded as it extends outwards, the darkening increasing almost imperceptibly, or it may be reduced to a mere chink by inward extension of the effect of RaC. The latter type is shown in the photograph reproduced in the 'Proc. R. Dublin Soc.,' vol. 13, Plate 3, fig. 1.

The appearance of the ring due to RaC, or the fourth ring, is at first a delicately shaded band, the shading being darker on the outer circumference. This corresponds to the steep descent of the Geiger or Bragg curve. Our opportunities of studying the distribution of ionisation along the track of a single  $\alpha$ -ray in mica are restricted to the rings due to RaC and ThC<sub>2</sub>. There seems to be no doubt that the essential features of the ionisation curve in a gas are reproduced in the mica.

Some outside radial dimensions of the fourth ring have been given above; they are typical. The values 0.0327 or 0.0328 are the best supported of the values read in this mica of Co. Carlow. It is very much alike with the readings obtained in the Cornish mica, and in the mica of Vagnay in the Vosges.

The final stage of growth of the uranium halo may be taken as that at which the outward expansion of the pupil has absorbed the third ring. The halo at this stage very often exhibits the appearance of a large and very dark pupil surrounded by an almost uniform penumbra-like band representing the effects of RaC. The last four haloes in the Table given below are of this character. In the other five haloes the darkening of the external ring has not extended inwards to meet the pupil. Its inner radius is denoted by R<sub>1</sub>. The haloes in this Table may be described as showing the final state of a uranium halo before every feature disappears in blackening which extends out to the limits attained by RaC.

The measurements contained in the Table are not quite so available as those already given, on account of the fact that the correction for the nucleus must be guess-work. I have made an allowance for it amounting to 0.0006 mm., that is I have assumed the nuclear radius to be 0.0012 mm.

		Pupil.	$R_1$ .	R.
1	Carlow	0.0230	0.0282	0.0340
$\frac{2}{3}$	,,	0.0230	0.0279	0.0341
3	,,	0.0226	0.0285	0.0340
4	,,	0.0224	0.0285	0.0334
$\frac{4}{5}$	.,	0.0214	0.0273	0.0333
6	,,	0.0221		0.0327
7	,,	0.0225	*	0.0330
8 9	Vosges	0.0215		0.0323
9	,,	0.0221		0.0327
		0.0223		0.0333

Table IV.—Uranium Haloes: Final Stage.

This final stage is depicted in the drawing, Plate 1, fig. 4. It will also be found in the photographs already referred to.

#### The Emanation Halo.

Haloes are found in considerable numbers in the Carlow mica, which consist of a solitary ring showing no detail whatever within, and which are only clearly distinguished from the first ring of the uranium halo by their dimensions. They vary in appearance much in the same manner as does the embryonic uranium halo. That is to say, some show a greater degree of darkening than others. They may present the appearance of a delicate smoke-coloured ring, or be more or less darkened within, the original ring appearing as a still darker border. They are often wonderfully sharp in outline. At an early stage they may show the faint development of the ring due to RaC, that is, of the fourth ring of the uranium halo. This fact at once attaches them to the uranium series of elements.

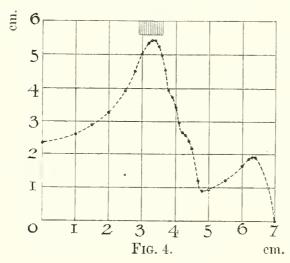
In later stages we find development progressing just as in the uranium halo. We may have the third ring as well as the fourth ring. The derivation of these haloes from the emanation can, of course, only be inferred when the inner structure is visible.

TABLE	·V	Emar	nation	Haloes.

	<i>r</i> <sub>1</sub> .	r.
$\frac{1}{2}$	$0.0139 \\ 0.0143 \\ 0.0146$	$ \begin{vmatrix} 0.0172 \\ 0.0176 \\ 0.0176 \end{vmatrix} $
4 5 6	0·0148 0·0143 0·0141	0·0176 0·0172 0·0172
7 8 9	0.0141 $0.0137$ $0.0141$	$ \begin{array}{c} 0.0172 \\ 0.0172 \\ 0.0172 \\ 0.0172 \end{array} $
10 11	0·0141 0·0141	0·0174 0·0174
	0.0142	0.0173

Mean radius of nucleus 0.0009 mm.

These results for the inner and outer radius of the emanation embryonic ring are, I think, very reliable. The measurements are comparatively easy. The question as to the allowance for the nucleus, however, presents some difficulty. As will presently be seen, there is evidence that these haloes originate by the occlusion of emanation on nuclei placed in veins or conduits in the mica. If the occlusion is a surface phenomenon, the entire nuclear radius should be deducted in order to ascertain the range. This has been done in the figures given in the Table. If the emanation was



absorbed throughout the nucleus, then the deduction should more correctly be half the radius. To make this correction, we may add half the mean nuclear radius to the mean values of  $r_1$  and r, as given at foot of the Table.

Fig. 4 shows the curve of ionisation in air of an emanation halo supposed to be formed in air. It is derived from emanation and its derivatives in exactly the same manner as fig. 1, and, as in the case of fig. 1, the added ordinates have been divided by 4 for convenience in plotting. I have shown just above the curve the location of the

originating ring-halo. The closest agreement is obtained on the supposition that the deduction for the nucleus is one-half the radius of the latter. The principles

according to which the halo in air and the halo in mica are compared are explained later. Fig. 6 is a drawing of the ring halo due to emanation to a scale of 800 diameters.

As already referred to, there is interesting evidence as to the origin of these haloes. They are—almost without exception—found located on cracks or veins in the mica. I have in another place\* referred to the conduits in this mica. These conduits undoubtedly contained radioactive materials. They are bordered by radioactive staining in a manner resembling the artificial halo of RUTHERFORD, which also is an emanation halo. The border may be very faint or very dark. Its radial extension is in general very much the same as that of the first ring of the uranium halo. And in many cases we can quite easily detect that the border is due to a succession of minute haloes whose centres are set close together along the conduit. The border in these cases consists, in fact, of a number of overlapping circles or rings, having approximately the radius of the first ring.

But every here and there one of the larger rings—the originating ring of the emanation halo—is found among the others. Examination shows in such cases a nucleus extending into the conduit, consisting of a refracting particle. Some of these emanation rings may be attended with the ring of RaC and other features of the more advanced halo. Again, the emanation halo may occur upon a fine, hair-like crack in the mica, and otherwise unattended. Or we may find them ranged in a linear sequence, with the originating conduit barely detectable.

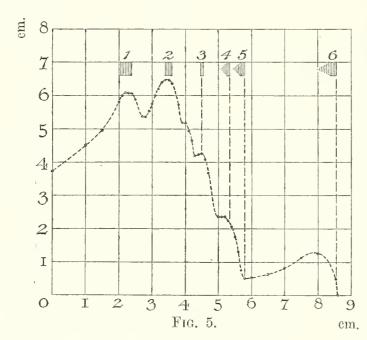
Nor is this the only evidence for the movement of radioactive materials in this mica. It is common to observe near the margin of a flake of the mineral, darkened veins, sometimes plainly following structural features of the mica, and branching at definite angles. Shapeless blotches of staining may attend these arborescent growths. Or the field may be strewn with elongated, sausage-shaped objects deeply stained. These appear to result from the coalescence of small spherical haloes, having the radius of the first ring, from 0.0137 to 0.0141 mm. These objects may attain the radial dimensions of more developed haloes. Thus, there may be an inner dark cylindrical core of radius 0.0190, and an outer cylindrical penumbra scaling 0.0327 mm. The entire structure may in some cases result from the entry of radioactive materials into a crack of short length, or from a succession of linearly arranged and closely approximating radioactive nuclei.

### The Thorium Halo.

If we investigate the formation of the thorium halo, assuming that a Geiger curve defines the ionisation due to each ray, in the manner already described in the case of the uranium halo, we obtain, as the resultant curve of ionisation due to the seven rays which go to form the halo, the curve given in fig. 5. The scale is the same as that of fig. 1. The ranges are those cited in Rutherford's 'Radioactive

<sup>\*</sup> Huxley Lecture at the University of Birmingham, 1912.

Transformations.' The ordinates for the ray ThC are reduced to one-third their full value, and those of ThC<sub>2</sub> to two-thirds their full value. This is done because it



seems probable that ThC is transformed in two distinct ways, only one-third the transforming atoms giving rise to  $\alpha$ -rays having the range 4.8 cm. The remaining two-thirds, after losing a  $\beta$ -ray, give rise to ThC<sub>2</sub>, which in breaking up emits rays of the range 8.60 cm.

The ionisation curve shown in fig. 5 is such a curve as a stream of parallel rays would give rise to. When we divide the ordinates by the squares of the abscissæ, we get the curve fig. 6. This last curve represents a very thin section of a halo taken through the centre of the halosphere, assuming that there was no in-

fluence counteracting the effect of the outward spread of the rays. Finally, fig. 7 shows the last curve corrected for perspective in the case of a section taken symmetrically about the centre of the halo-sphere, and 4 cm. thick.

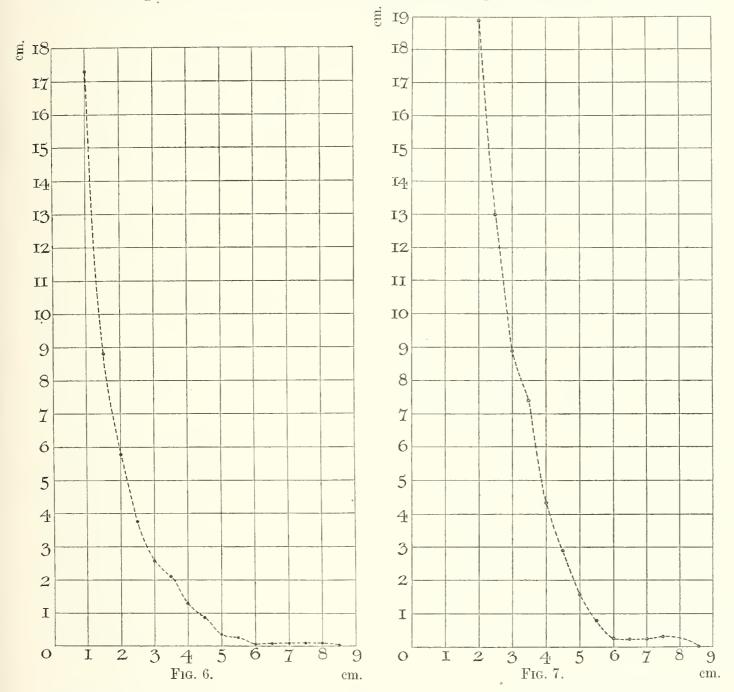
We shall now see, just as in the case of the uranium halo, that, while the last two curves might well represent the final appearance of the thorium halo, they fail to represent the stages of its development.

The first appearance of the thorium halo is that of two delicate rings, concentric one with the other. The area within the inner ring is generally more or less darkened. Occasionally, the darkening within the inner ring has obliterated the ring-like character of this first ring. That is, the first ring is merged in the general darkening. In other cases the ring shows a distinct band-like form, the radial width of the band being about 0.002 mm. I have never seen this first ring unaccompanied by the second ring. The second ring is rather indefinite upon its inner and outer boundaries. It often possesses a central, or almost central, darkening. It is convenient to take the measurements to this central darkening, for it is the best defined feature of the second ring. A clear space intervenes between the first and second rings. Fig. 7, Plate 1, is a drawing of an embryonic thorium halo to a scale of 800 diameters. The outer radial dimension of the inner ring is closely 0.0114 mm., and the radial distance of the central darkening of the second ring is about 0.0169 mm.

On a very few occasions a third ring has been seen. But its occurrence is so rare and its appearance so faint that I have little definite knowledge of it. One measurement placed the radial distance of its axis at 0.0219 mm. It may be of interest, however, to mention in connection with this ring that until I had sighted it the

existence of the shoulders or steps upon the ionisation curve, one of which apparently accounts for it, was unknown to me. This part of the curve had been put in with points spaced  $\frac{1}{2}$  cm. apart and it was only in trying to account for the ring that the rugosities on the curve were discovered.

The next stage of the thorium halo shows the first ring well darkened within and



often obliterated, the second ring somewhat more definite and connected with the first ring by a certain amount of staining, and the fourth ring, due to ThC<sub>2</sub>, appearing faintly encircling all. The drawing, fig. 8, shows the appearance of the halo at this stage.

The third stage which has come to my notice involves the obliteration of all the inner features within a deeply stained pupil. As in the case of all other halo-pupils the radial dimensions may be very various—in this case from 0.023 to 0.028; and,

doubtless, wider limits could be found. The pupil is simply the widening outwards of the halo under the influence of the ionisation, decreasing to the point of minimum effect. Outside the pupil the ring due to ThC<sub>2</sub> appears as a penumbra-like band. The accentuation of its extreme marginal boundary is, I think, less definite than in the case of the uranium halo. This may be due to the existence of a small number of rays which penetrate beyond the range of RaC<sub>2</sub>.\*

Table VII.—Dimensions of the Thorium Halo.

N		$r_1$ .	$r_2$ .	r3 (?).	Pupil.	R.
No.	Axis.	Outside.	Axis.	Axis.	Outside.	Outside.
$\begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix}$	0·0106 0·0100	0·0115 0·0115 0·0113	0·0168 0·0174	_	_	0.0402
4 5 6 7 8 9 10 11 12 13 14 15	0·0100 —————————————————————————————————	0.0113 $0.0115$ $0.0115$ $0.0115$ $0.0115$ $0.0117$ $0.0107$ $0.0115$ $0.0111$ $0.0113$ $0.0117$ $0.0111$	0.0170 $0.0168$ $0.0168$ $0.0168$ $0.0175$ $0.0174$ $0.0163$ $0.0166$ $0.0165$ $0.0176$ $0.0173$ $0.0170$	0.0219		0.0407
16 17 18		0.0110	0.0170	_	$0.0248 \\ 0.0267$	0·0400 0·0405
19					0.0256	0.0411
20	_				0.0274	0.0415
21					0.0281	0.0422
22	_	_			0.0243	0.0385
23	_			_	0.0250	0.0393
24		_		_	0.0263	0.0414
25	_	_		<u>-</u>	0.0248	0.0392
26	—			_	0.0269	0.0436
27		_		_	0.0231	0.0402
28	—		_	_	0.0250	0.0419
29		_	_	_	0.0273	0.0415
30	_	_		_	0.0255	0.0408
31	_	_	—	_	0.0255	0.0407
Means	0.0103	0.0114	0.0169		0.0257	0.0408

Nuclear radius varies from 0.0006 to 0.0013 mm.

Comparing the observed features of the thorium halo with those which might be expected if we assume the ionisation curve of fig. 5 to depict the development of the halo, we see that the first two rings are evidently accounted for by the maxima at

<sup>\*</sup> Rutherford and Wood, 'Phil. Mag.,' April, 1916.

about 2.2 and 3.5 cm. Their simultaneous development is explained by the nearly equal ionisation responsible for each; the somewhat greater ionisation of the outer maximum counteracting a certain amount of inward concentration recognisable in halo-development. The inner region of the first ring darkens up under the influence of the fairly strong ionisation shown within the first maximum. The somewhat uncertain third ring is probably referable to the prominence on the curve at 4.5 cm. The pupil may extend to a radial distance corresponding to 5.8 cm. Beyond this the penumbra due to ThC<sub>2</sub> appears.

We find, therefore, that the thorium halo develops in a manner quite in keeping with the form of the curve of ionisation in air representing the added activities of the known rays emitted by members of the thorium family. How far the location of the several observed features agrees with the ionisation curve will presently appear. I now quote some measurements made on thorium haloes in various stages of development. The haloes are all from the mica of Vagnay, Vosges. The dimensions under  $r_1$  refer to the first ring. A few readings to the axis of the ring are given. Most of the readings are taken to the outside boundary, this being the most definite feature of the ring. The readings applying to the second ring are in the column headed  $r_2$  and are taken to the central darkening; or, failing that, to the central line or axis of the ring as far as this can be estimated by eye. One reading to the centre of the third ring,  $r_3$ , is given. The radial dimension of the pupil in well darkened haloes is next given. These haloes vary much in depth of colour. The extreme boundary of the halo appears in the last column.

### Compound Uranium-Thorium Haloes.

It is well known that thorium-bearing minerals in most if not in all cases contain uranium. It might be expected, therefore, that the occurrence of compound haloes due to the joint action of the α-rays of both these families of radioactive elements would be frequent. In order the better to detect the presence of such haloes I plotted the ionisation curve due to an equal admixture of the parent substances. The distinctive feature of this curve was found to be the existence of a double outer ring: the outer ring due to ThC<sub>2</sub> containing within it the ring due to RaC. This was an easily recognisable feature. As regards internal features the second maximum, which is so conspicuous a feature of the thorium ionisation curve, is nearly obliterated. The compound halo would start with a strong ring at the distance of 2·3 cm. in air.

In the Leinster granite thorium minerals appear to be absent. But in the Vosges granite there are found side by side both thorium and uranium haloes. A careful watch for the compound halo was kept when examining this rock. However, only one quite definite example of a compound halo was observed. It was recognised by the double penumbra. The measured radii of the two rings were found to be quite correct; and as the strength of development was rather greater for the thorium ring it may be inferred that this substance predominated. Unfortunately the reference

to the position of this halo in the many slides in my possession was lost during the military occupation of Trinity College (and of my Laboratory) during the Sinn Fein rising in Dublin. I had intended obtaining a photograph of this halo or making a measured drawing of it.

It is probable that the scarcity of these compound haloes is to be referred to the generally great predominance of the thorium present, which has the effect of masking the effects of the uranium. This explanation is, however, not satisfactory in all respects.

### The Conversion Factor.

By this term I refer to the number which multiplied into the range in mica affords the equivalent range in air at pressure of 760 mm. and temperature of 15° C. The importance of this number is considerable. With it is involved the most interesting questions arising from the study of haloes.

We possess two methods of finding the range in a mineral equivalent to the range in air. We may calculate it on the basis of the chemical composition and density of the mineral according to laws determined by Bragg and Kleeman. Or we may determine it for any particular range if we are justified in identifying some feature of the halo as the result of a ray whose range in air is known.

Taking first the method by Bragg's Law, we find\* that 1 cm. in air of density 0.0012 corresponds to a range in the haughtonite of Co. Carlow of 0.000473 cm. This result is based on a chemical analysis of this mica, and a careful determination of its density. A small correction may be made to bring it into comparison with the tabulated ranges in air of the temperature 15° C. The density is 0.00122 at this temperature and at standard pressure. The equivalent range then becomes 0.000482 cm. The reciprocal of this number gives the factor which multiplied into the range in the mineral gives the range in air. We may write the conversion factor as

$$2075.$$
 (1)

When we refer to the halo itself for the conversion factor we assume that the connection between the ionisation and the velocity is the same in the mica as it is in a gas in so far that the maximum of ionisation is attained in both cases when the velocity has fallen to the same fraction of its original value.

Beginning with the integral curve of ionisation for the thorium family of elements, and comparing it with the measurements of thorium haloes in various stages, we find on the curve, fig. 5, two very prominent maxima at small radial distances from the centre. Outside the second appears a steep decline of the ionisation curve with two steps near its upper part and a pronounced step lower down. Then we have a minimum of ionisation which rises outwards to the blunt maximum due to ThC<sub>2</sub>. In Table VII we find first a ring or band of a radial width about one-fifth the

<sup>\* &#</sup>x27;Phil. Mag.,' April, 1910, p. 631.

radius; next a narrow shaded ring. Another ring sometimes succeeds. Then we have the somewhat variable limit of the pupil which we find developed on haloes darkened up within. Lastly comes the outer ring generated by the rays of ThC<sub>2</sub>.

If we lay out on millimetre paper the mean readings given in the Table along a line and enlarge them all proportionately by the usual construction involving the properties of similar triangles we find that when the radius for the second ring has attained the radial dimension of 3.5 cm., and so comes into agreement with the distance of the second prominence on the curve from the axis of Y—that is, with the radius of a second ring supposed generated in a halo in air—then the other readings at foot of the Table fall into the numbered positions shown above in fig. 5.

Examination of this figure shows that the agreement of the measurements with the features of the curve is very satisfactory. The outside radius of the first ring falls at 2.4 cm., which is just about where it might be expected. The third ring (numbered 3) is less definite. It seems to refer to the conspicuous prominence on the slope. The average pupil radius (marked 4) corresponds to the next conspicuous prominence. It may extend to anywhere on the lower slope leading down to the marked minimum of ionisation. The readings for the pupil radius, rising to 0.028 and 0.027, which are common readings in well-blackened haloes, place the outside limits of the pupil at 5.8 cm. from the centre (marked 5)—that is exactly at the foot of the downward slope. Similarly, the average reading for the extreme radius of haloes (about 0.0408 mm.) corresponds closely to 8.6 cm. radius of the halo in air. Extreme readings reach to the very foot of the curve. It is evident that the agreement between the measured and the theoretical features is extraordinarily close considering the difficulties attending the measurements. Quite possibly there is some chance involved in such agreement. But even if we were presented with a lesser degree of correspondence we would be entitled to conclude, as I think, that the integral curve of ionisation in a gas is certainly intimately connected with the mode of generation of the thorium halo.

Assuming this, we now find that if the radial dimension of the second ring, that is 0.0169 mm., corresponds to 3.5 cm. in air, we get as the conversion factor

$$2071.$$
 (2)

This same conversion factor, obviously, applies to the several features of the thorium halo with considerable accuracy.

The foregoing results appear to be so mutually consistent that we must, I think, ascribe considerable weight to the derived conversion factor. It is important to determine if there is any notable difference in the stopping power of this mica and that of the haughtonite of Ballyellen, Co. Carlow. It would seem as if there was but little, if, indeed, any at all. Uranium haloes, suitable for measurement, are not very common in the Vagnay mica. Here, however, are eight which permitted of correction for the nucleus and were well and clearly defined.

#### TABLE VIII.

Pupil radius.	R.
0.0215	0.0323
0.0212	0.0327
0.0217	0.0332
0.0230	0.0336
0.0230	0.0319
0.0204	0.0332
0.0219	0.0326
0.0190	0.0327
prompt of the contract published to	that someone
0.0215	0.0328

These results do not differ from the dimensions read in the Co. Carlow mica. We must compare them with the haloes of Table III (ante) rather than with those of Table IV, in which the ionisation has gone so far that the nucleus is no longer visible. The mean results are practically identical with those of Ballyellen. For some reason the Vosges uranium haloes do not exhibit the detail of the Carlow haloes. I have only once seen the third ring separated from the pupil in the former mica. The haloes of the Table given above and those of Table III appear to be in the same stage of development. I conclude that the conversion factor which applies to the Vosges mica applies also to the Ballyellen mineral.

We shall next examine the emanation halo. The counterpart of this halo in air exhibits a conspicuous maximum, which may be taken to attain its highest point at a distance from the centre of 3.35 cm.

The ring-shaped embryonic halo, which I have explained as due to nuclei occluding emanation of radium, measures on its outside radius in haughtonite 0.01734 mm., and on its inner radius 0.0142 mm. The mean radius is 0.0157. Upon these figures I venture to place considerable confidence. They have been carefully checked. The outside dimension of this halo is particularly easy to measure. It is generally sharp in outline. The inner radius is less easy to deal with, but as each reading in the Table is the mean of two or more readings which do not differ much among themselves, I think that in the general mean confidence may be placed.

When the mean radius as above is divided into 3.35 cm. we get the conversion factor as 2134. As regards the outlying part of the curve, that due to RaC, it is sufficient to say that the readings applying to it differ in no way from those obtained from the ordinary uranium halo. The same remark may be made to intervening features. But it is not always possible to say whether a particular halo has started with the emanation or with uranium.

I have given already (fig. 4) the ionisation curve in air proper to this halo, with the generating halo-ring marked in its correct position, assuming that the conversion factor is 2075. There is not perfect agreement. The conversion factor required to bring about agreement is sensibly larger than is required for the thorium haloes of the Vagnay mica. But this may be due to the assumption that the radioactive substance is carried on the surface of the nucleus. If the correction for the nucleus is taken as half the nuclear radius a fairly close agreement is obtained between the range in air and in mica, assuming the conversion factor 2075. The difficulty remains in effecting this reconciliation that it is hard to imagine the sufficiently rapid absorption throughout the nucleus of the short-lived emanation.

We shall next examine the uranium haloes of the Ballyellen haughtonite. The outer radius of well advanced haloes cannot differ much from 0.0334 mm. (Table IV). Dividing this into the range in air, i.e. into 6.94, we get the conversion factor as 2077. This is in good agreement with the conversion factor of the Vagnay mica. Multiplying 0.0334 into 2075 we get for the limit of the uranium halo the feature numbered 5 in the ionisation curve, fig. 1.

The next marked characteristic of the uranium curve is the minimum of ionisation at the distance 5.8 cm. in air. In Table IV we find that in well advanced haloes the pupil scales 0.0230. In these haloes we can seldom measure the nucleus. The value given, however, cannot be far wrong, for the outer radius of the third ring may extend to 0.0228 (Table III). Here the nuclear allowance is assured. We know that the final stage means a still further advance outwards. If now we take 0.0230 and divide it into 4.8 cm. we get 2086 as the conversion factor. How closely this is in agreement with the ionisation curve in air appears when we apply the conversion factor 2075. This places the extreme development of the pupil in the position marked 4 in fig. 1.

The external radius of the third ring is at 0.0216, about, according to the results of Table III. Applying the conversion factor 2075, we find the third ring located in the position numbered 3, fig. 1. Plainly it is in correspondence with the prominence on the curve at 4.3 or 4.4 cm. Using the same factor I give the location of the third ring as measured on the complex haloes of Table II. In this case we deal with the axial radius of the ring. It falls at 4.25 cm., and is evidently in agreement with the already determined position of the third ring.

The second ring, which has only been found in a few haloes, but which is a perfectly clear and definite feature, is apparently associated with the prominence on the ionisation curve at 3.5 cm. If we apply to the axial radius of this ring (0.0172) the conversion factor 2075, we find it in the locus marked 2 in fig. 1. This is too much to the right.

The last feature left to consider is the originating or first ring. It seems impossible to disassociate this ring from the marked ionisation maximum of the integral ionisation curve. As the result of very many measurements it has been found that the outer edge of the ring is 0.0142 mm. from the centre and the inner 0.0105 mm. The latter radius can hardly claim to be as accurately determined as

the former. It is more difficult to measure. But it will be noticed that the ratio  $(r-r_1)/r$ , derived from the Table, is in agreement with the results of investigation with use of high magnification as referred to on p. 61.

The integral ionisation curve, which has been very carefully plotted, would refer the axis of the ring to a radial distance of 2.2 cm. from the centre of the halo. But the axis of the first ring in mica is at a radial distance of 0.0124 mm. from the halo-centre. Dividing this into 2.2 cm. we get for the conversion factor 1774.

The first ring is, then, too great in radius to fit the curve of integral ionisation in air. Nor do I believe it possible by any allowance for the nucleus or refinement on the measurements to bring them into agreement.

Taking the conversion factor as 2075, which, as we have seen, is supported by Bragg's Law and by every feature of the thorium halo, and approximately by several of the uranium halo, we find the first ring to be located in position 1 in fig. 1. The conspicuous and abundant presence of this ring forbids us to ascribe it to any minor feature of the ionisation curve. Nor have we any other feature to which to refer the origination of the halo. It is plainly a primary feature. And within the boundary of this ring no trace of any other distinct feature has been observed. Irregular staining has been seen occasionally, adjacent to the nucleus, but such is not alone variable and irregular in dimensions; it may be, and generally is, entirely absent.

### Conclusion.

As the result of a very large number of measurements we find that the structure of the halo is determined by the added ionisation effects of all the  $\alpha$ -rays concerned in its genesis. A simple addition of the ordinates representing the ionisation of each ray serves to define the location of every feature of the thorium halo. Not one feature of this halo has been discovered which may not be referred to the features of the integral curve of ionisation proper to this family of radioactive elements. The relative spacing of the features of the halo fits with satisfactory accuracy the features of the curve. The only criticism here is that the first and second rings are a little too widely separated. But the departure from perfect fit is so small that we would not be justified in laying any stress upon it unless we were assured of a higher order of accuracy in all the constituent elements entering into the matter than we are at present entitled to assume.

This close interfit of the halo in air and the halo in mica gives us a conversion factor which agrees very nearly with that derived independently on the additive law discovered by Bragg for a mica which exhibits very similar stopping power to that containing the thorium haloes.

Applying this conversion factor to the ionisation curve for uranium haloes we find, indeed, that the outer features of the uranium halo exhibit fairly satisfactory interfit with the halo in air. But the inner features do not. The first and second rings appear to be displaced outwards. Both these features are

measured with a considerable degree of accuracy and I do not think there is any doubt of the misfit. The emanation halo, which is also measurable with reliable accuracy, shows a small misfit in the opposite sense; the halo-radius in the mica being too small for the halo-radius in air. But in this case I have assumed that the a-rays leave the very surface of the nucleus, and I have accordingly deducted the entire radius of the latter. This assumption may not be justified. If the emanation became deeply absorbed in the nucleus a lesser deduction would be correct. The mean nuclear radius is 0.0009 mm. Restoring one-half this to the radial measurements of the halo we find that its axial radius falls at 3.36 cm. assuming the conversion factor 2075. This gives good agreement. In short we are not in a position to lay stress upon the apparent misfit in the case of this halo.

We are entitled to ask for the possible explanation of the misfit of the inner features of the uranium halo. The easiest answer would obviously be that some addition to our knowledge of the ionisation curve was required which would have the effect of modifying the inner features of the curve. The ionisation curve of U<sub>1</sub> and U<sub>2</sub> has been investigated by Geiger and Nuttall\* and found to agree in range with what would be expected from the logarithmic law connecting the range with the transformation constant. There would, therefore, appear to be no room for error here. If, then, the discrepancy is to be sought in the plot of the halo in air it would seem as if we must look for some element at present omitted from the series. But we are in the difficulty that the introduction of such an element must disturb the transformation constants of the recognised elements and these transformation constants have been found to be in good agreement with the logarithmic law already referred to.

The only other suggestion I can offer is that of an actual change in the range of the  $\alpha$ -rays, since the remote period when the haloes were formed. The age of the Co. Carlow (Ballyellen) rock is late Silurian or early Devonian; that of the Vagnay rock, Carboniferous (pre-Stephanian), or possibly very much older. The Cornish granite is Carboniferous in age. We would have to assume that the ranges of the uranium rays were formerly longer than they now are, or that a proportion of uranium atoms then existed having a longer range. As we know that isotopic elements may possess very various radioactive properties, there does not seem to be any objection to this hypothesis from the chemical point of view, the atoms of longer and shorter range quite possibly obeying the same chemical influences in the processes attending magmatic differentiation.

This view would involve, of course, the transformation constants: the atoms of longer  $\alpha$ -range possessing the shorter longevity. We are not in a position to state that the observed discrepancy between the ranges inferred from the halo in mica and those recognised to-day in air is confined to the early uranium atoms. The observations suggest that the radioactive properties of atoms derived from the latter

<sup>\* &#</sup>x27;Phil. Mag.,' March, 1912.

may have differed from those known to-day. There must certainly have been a convergence towards the properties of the existing shorter-lived members of the series, for the outer parts of the halo are in fair agreement with the recognised ranges of the final products of transformation.

According to the relation discovered by Carruthers,\* the range is numerically proportional to a certain power of the atomic weight. If, then, the radioactive losses sufficed to lead the former line of radioactive descent through existing atomic weights, it might possibly be the case that abnormalities in the ranges of the earlier members of the series might not appear in the later products of change.

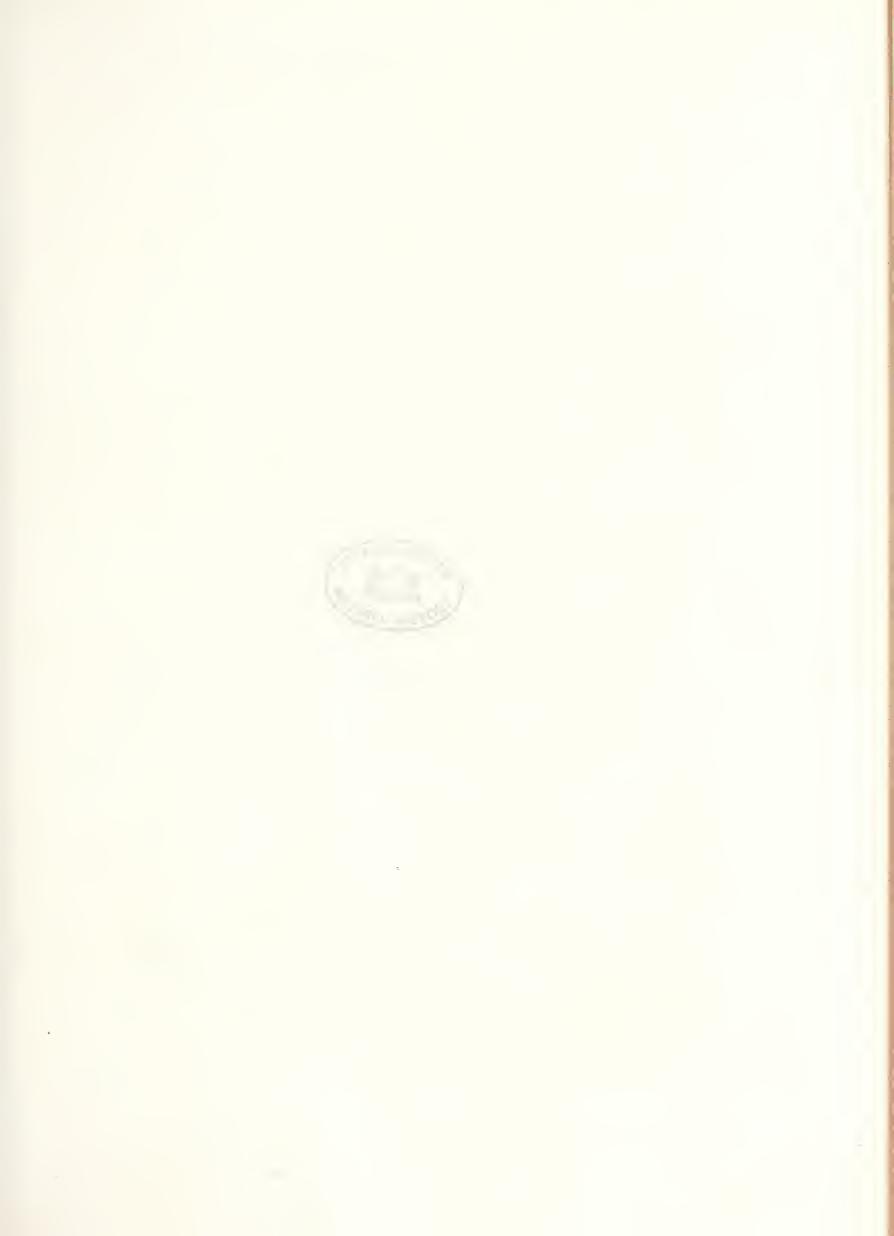
It may be urged that, if there had been a gradual change progressing in the average range of certain of the α-rays, this should be revealed in a want of definition of the embryonic haloes. The answer to this is that such an effect would be very difficult to detect. It may be that the inward widening of the embryonic band has been influenced in this manner. We possess no standard for comparison. We have no means of deciding between what might have been due to a convergence in the ranges of the rays and what might be due to development in accordance with the form of the curve. Nor can we determine in how far the observed amount of imperfection in the definition is due to the one cause or to the other. Evidence in this direction—that is, from the actual appearance of the haloes presented to us from rocks of any age—seems, unfortunately, to fail us.

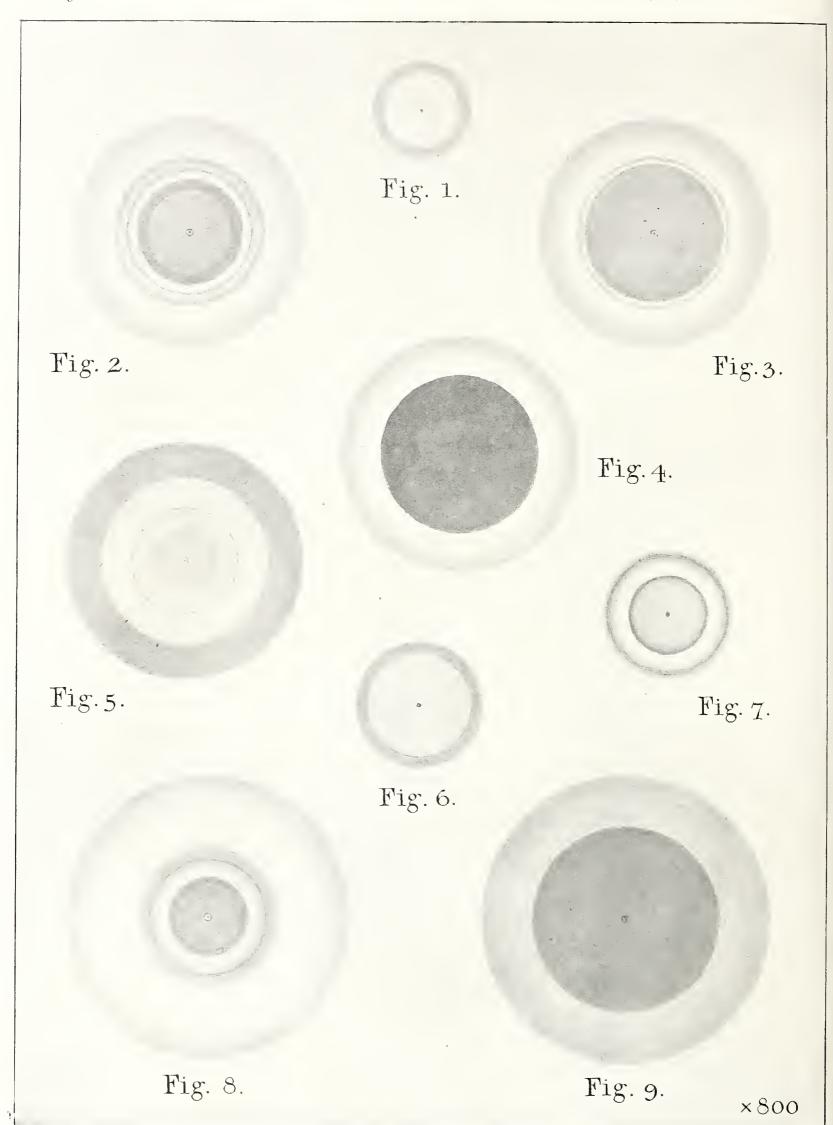
RUTHERFORD, in discussing the origin of actinium,† has remarked on the possibility that radioactive change may give rise to simultaneously formed products of different atomic weight, periods, etc. If we supposed uranium to be derived from some antecedent element, the original uranium may well have possessed different radioactive properties for similar reasons. The shorter-lived atoms would get scarcer during geological time, and there would be a convergence in the value of λ, which may be still going on. Such may have been the history or evolution of many of the really or apparently stable elements. Indeed, in discussing the law of Geiger and Nuttall, Rutherford has advanced a theoretical explanation for the relation between range and longevity, which would seem to have bearings on the views I am stating. The short range is due to the gradual waste of energy by radiation during long periods of time.

The high lead ratio of uranium-bearing minerals would find explanation on the view that there was a more rapid decay of early uranium atoms, or, rather, that a large number of uranium atoms formerly transformed at a more rapid rate than the value revealed by present-day observation. Similarly, if thorium gives rise ultimately to lead—as seems probable—the scarcity of lead in thorium-bearing ores is in perfect harmony with the close agreement between the past and present ranges of the α-rays emitted by members of this series. It is almost unnecessary to

<sup>\* &#</sup>x27;Nature,' January 20, 1916.

<sup>† &#</sup>x27;Radioactive Substances and their Transformations,' p. 522.





point out that discrepancy between results obtained on radioactive and geological data in the evaluation of geological time would disappear if the present views have any foundation.

It is quite evident that we have at present no source but the halo from which information of the kind we are discussing can be obtained. At this early stage in the study of haloes, it may seem premature to offer such far-reaching suggestions as I have ventured upon above. The answer is obvious. The incentive to careful study of haloes formed in rocks of different ages increases with the issues at stake. Such studies are very desirable. If, in recent materials, the originating uranium halo could be found, we might at once decide whether the Silurian or Devonian haloes we have been considering showed a real discrepancy between existing and past ranges of the \alpha-rays, or whether we must seek some other explanation of the observa-My own efforts to apply this criterion have so far not been successful, although a large number of micas have been examined. The reasons seem to be that very small nuclei alone afford the requisite definition. Now small nuclei contain little radioactive material, and, consequently, either because the time is too short or the rate of decay is now too slow, a uranium-bearing nucleus in a recently formed mineral may rarely or never afford the embryonic halo. In tertiary granites—as, for instance, that of the Mourne Mountains—the haloes lack the detail and delicacy of the more ancient haloes. The nuclei are large and the darkening around them fuzzy and indefinite. Here, however, the nature of the medium is partly to blame. Similar discouragement has been encountered in other recent materials; but it may be that further search may be rewarded with haloes which will reveal decisive evidence on the points at issue.

### DESCRIPTION OF PLATE.

Fig. 1.—Uranium halo. First stage.

Fig. 2.—Developing uranium halo. Second stage, showing Rings 1, 2, 3 and 4.

Fig. 3.—Uranium halo. Third stage, showing development of third ring.

Fig. 4.—Uranium halo. Fourth stage.

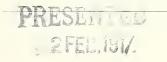
Fig. 5.—Reversed uranium halo.

Fig. 6.—Radium emanation halo. First stage.

Fig. 7.—Thorium halo. First stage.

Fig. 8.—Thorium halo. Second stage.

Fig. 9.—Thorium halo. Third stage.





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A Detailed Study of the Enumeration of the Partitions of Multipartite Numbers.

By Major P. A. MACMAHON, R.A., D.Sc., Sc.D., F.R.S.

Received April 13,—Read May 11, 1916.

#### Introduction.

In this paper I give the complete solution of the problem of the partition of multipartite numbers. This is the same subject as that named by Sylvester, "Compound Denumeration." Twenty-nine years have elapsed since I announced that the algebra of symmetric functions is co-extensive with the grand problems of the combinatory analysis. The theory of symmetric function supplies generating functions which enumerate all the combinations, while the operators of Hammond\* are the instruments which are effective in actually evaluating the coefficients of the terms of the expanded generating functions. When these operators fell from the hands of Hammond, they were already of much service as mining tools in extracting the ore from the mine field of symmetric functions; but they were only partially They required sharpening and general adaptation to the work in hand. The first step was to decompose an operator of given order into the sum of a number of operators in correspondence with every partition of the number which defines the order. Since there is a Hammond operator corresponding to every positive integer, this process resulted in there being an operator in correspondence with every partition of every integer. The outcome of this decomposition was that the operators were able to deal with the symmetric operands in a much more effective manner. The surface material of the mine could not only be removed, but the strata to a considerable depth could be dealt with. But this was not sufficient. It became necessary to effect a further decomposition by showing that every partition operator could be represented by a sum of composition operators. There emerged a composition operator in correspondence with every permutation of the parts of the partition of the operator. The operators at once became effective in dealing with the material in the lower strata of the mine field. The operators had, in fact, been handled with particular reference to the operands with which they were to be associated. It was now necessary to deal with the material of the mine with particular reference to the tools which had

<sup>\* &#</sup>x27;Proc. Lond. Math. Soc.,' 1883, vol. xiv., pp. 119-129.

been forged. To evaluate the coefficients we have to operate repeatedly with the appropriate operators until a numerical result is reached. In order to accomplish this with facility and to establish laws we have to put the generating functions in such a form that these operations are carried out in a regular and simple manner. To make my meaning clear, I will instance the case of the simple operation of differentiation  $\partial_x$  and the exponential function  $e^{ax}$ . We have

$$\partial_x e^{ax} = \alpha e^{ax},$$

the effect of the operation being, to merely multiply the operand by the numerical magnitude  $\alpha$ .

Thence

$$\partial_x^n e^{ax} = \alpha^n e^{ax}$$

and we arrive at the conclusion, that if a given operand, a function of x, could be expressed as a linear function of exponential functions of x, the r times repeated operation of  $\partial_x$  could take place with facility upon each term of the linear function, and a general law for the repeated operation of  $\partial_x$  upon the operand would be obtainable. This reflection suggests the possibility of finding symmetric function operands in a form which will enable the repeated performance of Hammond's operators in a practically effective manner. It is quite certain that any such operand must possess at least two properties in common with the exponential function: (i) its first term must be unity; (ii) it must contain an infinite number of terms. The first step was to find a symmetric function  $\mathbb{Q}_1$  of the elements a,  $\beta$ ,  $\gamma$ , ... such that the effect of every Hammond operator upon it is to leave it unchanged; or, as I prefer to say, to multiply it by unity.  $\mathbb{Q}_1$  is, in fact, the sum of unity and the whole of the monomial symmetric functions  $\mathbf{\Sigma} \alpha^p \beta^q \gamma^k \dots \equiv (pqr \dots)$ . It is in the partition notation

$$\mathbf{Q}_1 = 1 + (1) + (2) + (1^2) + (3) + (21) + (1^3) + \dots$$
 ad inf.

It was then found that the effect of any Hammond operator upon any power of  $\mathbb{Q}_1$  is merely to multiply it by a positive integer. It then appeared that, denoting  $\mathbb{Q}_1$  by  $F(a, \beta, \gamma, ...)$ , the function

$$Q_i = F(a^i, \beta^i, \gamma^i, \ldots)$$

possesses properties of a character similar to those appertaining to  $\mathbb{Q}_1$ . The fact is that any Hammond operator when performed upon any power of  $\mathbb{Q}_i$ , say  $\mathbb{Q}_i^{k_i}$  has the effect of merely multiplying it by an integer, which may exceptionally be zero. Finally the important fact emerged that the performance of any Hammond operator upon the product

$$\mathbf{Q}_1^{k_1} \mathbf{Q}_2^{k_2} \dots \mathbf{Q}_i^{k_i} \dots,$$

where  $k_1, k_2, \ldots k_i, \ldots$  may, each of them, be zero or any positive integer, is merely to multiply it by a positive integer, which may, exceptionally, be zero

This discovery involves the complete enumerative solution of the unrestricted partition of multipartite numbers into a given number of parts. The reason of this is that the enumerating symmetric function generating function can be expanded in ascending powers of the functions  $\mathbf{Q}_1, \mathbf{Q}_2, \mathbf{Q}_3, \ldots$ . On every term of this expansion the repeated performance of Hammond operators is practically effective and is successful in forcing out the sought numerical coefficients. When the magnitudes of the integer constituents of the multipartite parts are restricted in any manner there exists similarly an appropriate series of symmetric functions,

$$U_1, U_2, \dots U_i \dots,$$

the formation of which is explained in the paper, which in their properties are analogous to the series  $Q_1, Q_2, \dots Q_n, \dots$ . This circumstance involves the complete enumerative solution when the magnitudes of the constituents of the parts are restricted in any manner whatever.

#### Section I.

#### The Partition of Multipartite Numbers.

Art. 1. One of the problems which has engaged the attention of writers on the combinatory analysis is that of enumerating the different modes of exhibiting a given composite integer as the product of a given number of factors. For instance, the number 30, which is the product of three unrepeated primes, can be given as the product of two factors in the three ways,

$$2 \times 15$$
,  $3 \times 10$ ,  $5 \times 6$ .

When the given composite number is a product of different primes the question is very easy and is completely solved by means of the generating function

$$1/(1-x)(1-2x)...(1-kx).$$

In the ascending expansions the coefficient of  $x^{q-k}$  is the number of ways of factorizing a number, which is the product of q different primes, into exactly k factors.\*

Generating functions of the same character have also been obtained for some other simple forms of the composite number such as  $p_1^2p_2 \dots p_q$ ,  $p_1^2p_2^2p_3 \dots p_q$ ;  $p_1$ ,  $p_2$ , ... denoting primes.

It is, of course, obvious that the absolute magnitudes of the prime factors have nothing whatever to do with the question, which necessarily appertains to the exponents of the primes and to nothing else.

<sup>\*</sup> Compare 'NETTO's Combinatorik,' 1901, pp. 168 et seq.

Art. 2. Writers upon the problem have not usually observed that the general question is identical with the partition of a multipartite number into a given number of parts. Thus the problem discussed by Netto and others is simply the enumeration of the partitions, into exactly k parts, of the multipartite number

1111 ... 
$$q$$
 times repeated.

Ex. gr. when q = 3, k = 2 (see the two-factor factorization of  $2 \times 3 \times 5$  above), we have three partitions of the multipartite 111 into exactly two parts. These partitions are

(110, 001), (101, 010), (011, 100).

In general the enumeration of the factorizations, involving k factors, of the composite number

$$p_1^{m_1}p_2^{m_2}\dots p_s^{m_s},$$

'yields the same number as the enumeration of the partitions of the multipartite number

$$m_1 m_2 \dots m_s$$

into exactly k (multipartite) parts.

Art. 3. It is the same problem also to enumerate the separations of a given (unipartite) partition. Thus in relation to the partition (321) of the number 6, there is a one-to-one correspondence between the separations which involve two separates and the partitions of the multipartite number 111, which involve exactly two parts.

The separations are in fact

In general there is a one-to-one correspondence between the separations of the partition

$$(q_1^{m_1}q_2^{m_2}\dots q_s^{m_s}),$$

which involve k separates, and the partitions of the multipartite number

$$m_1m_2 \ldots m_s$$

which involve exactly k parts.

Art. 4. The general question of multipartite partition I have already discussed\* by a method of grouping the partitions and a particular theory of distribution. The present investigation which depends upon other principles leads to results of a different and more general character. I showed many years ago† that in regard to the system of infinitely numerous quantities

$$\alpha, \beta, \gamma, \ldots,$$

<sup>\* &#</sup>x27;Phil. Trans. Camb. Phil. Soc.,' vol. xxi., No. xviii., pp. 467-481, 1912.

<sup>† &#</sup>x27;Proc. Lond. Math. Soc.,' vol. xix., 1887, pp. 220 et seq.

the enumerating generating function is the symmetric function

wherein if  $h_s$  denote the sum of homogeneous products of weight s of the quantities  $\alpha$ ,  $\beta$ ,  $\gamma$ , ..., the s-1<sup>th</sup> fractional factor of the generating function possesses a denominator factor corresponding to every separate term of  $h_s$ . The function is to be developed in ascending powers of  $\alpha$  and, replacing for the moment the series  $\alpha$ ,  $\beta$ ,  $\gamma$ , ... by  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ , ..., we seek the coefficient of

$$\alpha^k \left( \sum \alpha_1^{m_1} \alpha_2^{m_2} \dots \alpha_s^{m_s} \right).$$

We write this, usually, in the notation

$$a^k (m_1 m_2 \dots m_s).$$

The coefficient mentioned enumerates the partitions of the multipartite number

$$(m_1m_2\ldots m_s),$$

into k or fewer parts. If the first fractional factor 1/1-a had been omitted the coefficient would have denoted the number of the partitions into exactly k parts. The inclusion of the factor 1/1-a is of great importance to the investigation and equally yields the enumerations into exactly k parts, because from the coefficients of  $a^k (m_1 m_2 \dots m_s)$  we have merely to subtract the coefficients of  $a^{k-1} (m_1 m_2 \dots m_s)$ . The importance is due to the circumstance that the symmetric functions which present themselves in the expansion are in the best possible form for the performance of the Hammond operators. This is not the case when the factor 1/1-a is excluded, as then a transformation, the necessity for which is not at once clear, is needed to obtain the proper form.

I will remind the reader that, writing

$$(1-\alpha x)(1-\beta x)(1-\gamma x)... = 1-a_1x+a_2x^2-a_3x^3+...$$

Hammond's differential operator of order m is

$$\mathbf{D}_{m} = \frac{1}{m!} (\partial_{a_1} + \alpha_1 \partial_{a_2} + \alpha_2 \partial_{a_3} + \dots)^{m};$$

and its cardinal property is

$$D_{m_1}D_{m_2}...D_{m_s}(m_1m_2...m_s)=1;$$

and this operation does not result in unity, when it is performed upon any other symmetric function.

In order to obtain the coefficient of

$$a^k (m_1 m_2 \dots m_s),$$

in the expanded function, we first of all find the complete coefficient of  $\alpha^k$  and then operate upon it with the Hammond combination of operators

$$D_m D_m \dots D_m$$
.

The result is an *integer* followed by the sum of an infinite series of symmetric functions. The integer mentioned is the number we seek.

Art. 5. We now expand the generating function. On well-known principles we can assert that the coefficient of  $a^k$  in the expansion is the homogeneous product-sum of order k of unity, and of the whole of the  $\alpha$ ,  $\beta$ ,  $\gamma$ , ... products which occur in the denominator factors of the generating function. The elements, of which we must form homogeneous product sums are, in fact,

$$\alpha, \beta, \gamma, \ldots,$$
 $\alpha^2, \beta^2, \gamma^2, \ldots \alpha\beta, \alpha\gamma, \dot{\beta}\gamma, \ldots,$ 
 $\alpha^3, \beta^3, \gamma^3, \ldots \alpha^2\beta, \alpha^2\gamma, \ldots \alpha\beta\gamma, \alpha\beta\delta, \ldots$ 

We can form these product-sums from the sums of the powers of these elements, because we have before us the well-known symmetric function formula

$$h_k = \sum_{\sigma} \frac{s_1^{k_1} s_2^{k_2} \dots s_i^{k_i}}{1^{k_1} 2^{k_2} \dots i^{k_i} k_1! k_2! \dots k_i!}.$$

The sum of the powers are readily formed; for, calling them

$$Q_1, Q_2, \ldots Q_i, \ldots,$$

it is clear that  $\mathbb{Q}_i$  is the sum of unity and the whole of the monomial (that is to say merely involving in the partition notation a single partition), symmetric functions of weights one to infinity. Hence

$$\mathbb{Q}_1 = 1 + (1) + (2) + (1^2) + (3) + (21) + (1^3) + \dots$$
 ad inf.;

and, regarding  $\mathbb{Q}_1$  as  $F(\alpha, \beta, \gamma, ...)$ , it is obvious that

$$\mathbb{Q}_i = \mathbb{F}\left(\alpha^i, \, \beta^i, \, \gamma^i, \, \ldots\right);$$

showing us that

$$\mathbf{Q}_2 = 1 + (2) + (4) + (2^3) + (6) + (42) + (2^3) + \dots,$$
  
$$\mathbf{Q}_i = 1 + (i) + (2i) + (i^2) + (3i) + (2i, i) + (i^3) + \dots.$$

Thence the expansion

$$\begin{aligned} & 1 + a \mathbf{Q}_{1} \\ & + \frac{a^{2}}{2!} (\mathbf{Q}_{1}^{2} + \mathbf{Q}_{2}) \\ & + \frac{a^{3}}{3!} (\mathbf{Q}_{1}^{3} + 3 \mathbf{Q}_{1} \mathbf{Q}_{2} + 2 \mathbf{Q}_{3}) \\ & + \frac{a^{4}}{4!} (\mathbf{Q}_{1}^{4} + 6 \mathbf{Q}_{1}^{2} \mathbf{Q}_{2} + 3 \mathbf{Q}_{2}^{2} + 8 \mathbf{Q}_{1} \mathbf{Q}_{3} + 6 \mathbf{Q}_{4}) \\ & + \dots \\ & + a^{k} \mathbf{F}_{k} (\mathbf{Q}) \\ & + \dots \end{aligned}$$

$$\mathbf{F}_{k} (\mathbf{Q}) = \mathbf{\Sigma} \frac{\mathbf{Q}_{1}^{k_{1}} \mathbf{Q}_{2}^{k_{2}} \dots \mathbf{Q}_{i}^{k_{i}}}{\mathbf{1}^{k_{1}} \mathbf{Q}_{2}^{k_{2}} \dots \mathbf{Q}_{i}^{k_{i}}} \cdot \mathbf{E}_{k_{1}} \mathbf{Q}_{k_{2}} \cdot \mathbf{E}_{k_{2}} \cdot \mathbf{E}_{k_{3}} \cdot \mathbf{E}_{k_{4}} \cdot \mathbf{E}_{k_{5}} \cdot \mathbf{$$

where

Art. 6. The importance of this expansion lies in the fact that the infinite series of Hammond operators on the one hand and the infinite series of Q functions on the other hand have very remarkable properties in relation to one another. The first

property we notice is that from the well-known law of operation,

$$\mathbf{D}_{m}\mathbf{Q}_{1}=\mathbf{Q}_{1},$$

for all values of m. Also

$$D_{\mathbf{w}}\mathbf{Q}_{2}=\mathbf{Q}_{2}$$
, or zero,

ascending as m is, or is not, a multiple of two. And generally

$$D_m Q_i = Q_i$$
, or zero,

according as m is, or is not, a multiple of i.

When  $D_m$  is performed upon a product of k separate functions, it operates through the medium of a number of operators associated with the compositions of m into k parts, zero being regarded as a part and  $D_0$  being regarded as a symbol for unity. Thus the compositions of the number 4 into three parts being 400, 040, 004; 310,

301, 130, 103, 031, 013; 220, 202, 022; 211, 121, 112, the law of operation is as follows:—

$$\begin{split} D_{4}Q_{a}Q_{b}Q_{c} &= (D_{4}Q_{a})(D_{0}Q_{b})(D_{0}Q_{c}) + (D_{0}Q_{a})(D_{4}Q_{b})(D_{0}Q_{c}) + (D_{0}Q_{a})(D_{0}Q_{b})(D_{4}Q_{c}) \\ &+ (D_{3}Q_{a})(D_{1}Q_{b})(D_{0}Q_{c}) + (D_{3}Q_{a})(D_{0}Q_{b})(D_{1}Q_{c}) + (D_{1}Q_{a})(D_{3}Q_{b})(D_{0}Q_{c}) \\ &+ (D_{1}Q_{a})(D_{0}Q_{b})(D_{3}Q_{c}) + (D_{0}Q_{a})(D_{3}Q_{b})(D_{1}Q_{c}) + (D_{0}Q_{a})(D_{1}Q_{b})(D_{3}Q_{c}) \\ &+ (D_{2}Q_{a})(D_{2}Q_{b})(D_{0}Q_{c}) + (D_{2}Q_{a})(D_{0}Q_{b})(D_{2}Q_{c}) + (D_{0}Q_{a})(D_{2}Q_{b})(D_{2}Q_{c}) \\ &+ (D_{2}Q_{a})(D_{1}Q_{b})(D_{1}Q_{c}) + (D_{1}Q_{a})(D_{2}Q_{b})(D_{1}Q_{c}) + (D_{1}Q_{a})(D_{2}Q_{b})(D_{2}Q_{c}) \end{split}$$

 $D_0$ , being unity, may be omitted but has been retained above to make the connexion with the compositions quite clear. This method of performing  $D_m$  upon a product I have explained and used in previous papers during the last five and twenty years. Upon this example some observations can be made. In the first place the operation breaks up into 15 portions because the number 4 has 15 three-part compositions. The result of each portion must be moreover either  $Q_aQ_bQ_c$  or zero, because  $D_tQ_s$  is either  $Q_s$  or zero. Hence the result of the whole operation must be merely to multiply  $Q_aQ_bQ_c$  by some integer  $\geq 15$ . In general the result of the operation

 $D_m \mathbf{Q}_1^{k_1} \mathbf{Q}_2^{k_2} \dots \mathbf{Q}_i^{k_i}$ 

must be merely to multiply the product

$$\mathbf{Q}_1^{k_1}\mathbf{Q}_2^{k_2}\ldots\mathbf{Q}_i^{k_i}$$

by some integer equal to, or less, than the number of compositions of m into  $k_1 + k_2 + \ldots + k_i$  parts, zero always counting as a part.

Hence also the result of the operation

$$\mathbf{D}_{m_1}\mathbf{D}_{m_2}\ldots\,\mathbf{D}_{m_r}\mathbf{Q}_1{}^{k_1}\mathbf{Q}_2{}^{k_2}\ldots\,\mathbf{Q}_i{}^{k_i}$$

must be merely to multiply the product

$$\mathbb{Q}_1^{k_1}\mathbb{Q}_2^{k_2}\dots\mathbb{Q}_i^{k_i}$$

by an integer.

This valuable result shows that the Hammond operators may be performed with facility upon the function

 $\mathbf{F}_{k}(\mathbf{Q})$ 

which is before us.

Art 7. The determination of the result of the operation

$$\mathbb{D}_m \mathbb{Q}_1^{k_1} \mathbb{Q}_2^{k_2} \dots \mathbb{Q}_i^{k_i}$$

is now entered upon. We have to find the value of the multiplying integer

The value is clearly equal to the number of compositions of m which do not have the effect of multiplication by zero. Suppose that we write out the operand at length

$$Q_1Q_1Q_1 \dots Q_2Q_2Q_2 \dots Q_iQ_iQ_i \dots$$

in *i* blocks, containing  $k_1, k_2, \dots k_i$  factors respectively.

Underneath the k factors we will suppose written any composition of m into k parts, zero being included as a part.

In order that the corresponding operation may result in unity and not in zero we have the conditions:—

- (i.) Any number, including zero, may occur underneath any of the  $k_1$  factors  $\mathbf{Q}_1$ ;
- (ii.) Zero, or any multiple of 2, may occur underneath any of the  $k_2$  factors  $\mathbf{Q}_2$ ;
- (iii.) Zero, or any multiple of 3, may occur underneath any of the  $k_3$  factors  $\mathbf{Q}_3$ ;
- (iii....) And lastly, zero, or any multiple of i, may occur underneath any of the  $k_i$  factors  $\mathbf{Q}_i$ .

How many such compositions exist?

We have merely to find the coefficient of  $x^m$  in the expansion of

$$(1+x+x^2+\ldots)^{k_1}(1+x^2+x^4+\ldots)^{k_2}(1+x^3+x^6+\ldots)^{k_3}\ldots(1+x^i+x^{2i}+\ldots)^{k_i};$$

for this is the function which enumerates the compositions which possess these properties. In fact to form the composition we take a power of x from each of the first  $k_1$  factors; then a power of x from each of the next  $k_2$  factors, observing that the exponents of x are all zero or multiples of two; then a power of x from the next  $k_3$  factors, observing that the exponents are all zero or multiples of three; and so on, until finally in the  $k_i$  factors we find that the exponents are all zero or multiples of i.

Hence it follows that the operation

$$D_m \mathbf{Q}_1^{k_1} \mathbf{Q}_2^{k_2} \dots \mathbf{Q}_i^{k_i}$$

has the effect of multiplying  $\mathbf{Q}_1^{k_1}\mathbf{Q}_2^{k_2}\dots\mathbf{Q}_i^{k_i}$  by a number which is given by the coefficient of  $x^m$  in the expansion of

$$(1-x)^{-k_1}(1-x^2)^{-k_2}(1-x^3)^{-k_3}\dots(1-x^i)^{-k_i}$$
;

an elegant theorem.

Let this coefficient be denoted by

$$F_q(m; 1^{k_1}2^{k_2}\dots i^{k_i});$$

so that

$$\mathbf{D}_{m}\mathbf{Q}_{1}^{k_{1}}\mathbf{Q}_{2}^{k_{2}}\ldots\mathbf{Q}_{i}^{k_{i}}=\mathbf{F}_{q}\left(m\;;\;1^{k_{1}}2^{k_{2}}\ldots\;i^{k_{i}}
ight)\;.\;\mathbf{Q}_{1}^{k_{1}}\mathbf{Q}_{2}^{k_{2}}\ldots\mathbf{Q}_{i}^{k_{i}}$$

Art. 8. Looking to the symmetric function expressions of  $\mathbf{Q}_1$ ,  $\mathbf{Q}_2$ , ...  $\mathbf{Q}_i$  it will be noted that the only portion of the product

$$\mathbf{Q}_1^{k_1}\mathbf{Q}_2^{k_2}\,\ldots\,\mathbf{Q}_i^{k_i}$$

which does not involve the elements  $\alpha, \beta, \gamma, \dots$  is unity.

Hence the portion of

$$D_m \mathbf{Q}_1^{k_1} \mathbf{Q}_2^{k_2} \dots \mathbf{Q}_i^{k_i}$$

that is free from the elements is

$$F_{\sigma}(m; 1^{k_1}2^{k_2}\dots i^{k_i}),$$

which is obtained directly from the result of the operation by putting

$$\mathbf{Q}_1 = \mathbf{Q}_2 = \ldots = \mathbf{Q}_i = 1.$$

We may represent this circumstance by the convenient notation

$$(D_m \mathbf{Q}_1^{k_1} \mathbf{Q}_2^{k_2} \dots \mathbf{Q}_i^{k_i})_{\mathbf{Q}=1} = F_q (m; 1^{k_1} 2^{k_2} \dots i^{k_i}).$$

The number of partitions, of the unipartite number m, into k or fewer parts, is by the present investigation

$$\begin{split} & \mathcal{D}_{m} \mathcal{F}_{k} \left( \mathbf{Q} \right)_{\mathbf{Q} = 1} \\ &= \boldsymbol{\Sigma} \frac{\left( \mathcal{D}_{m} \mathbf{Q}_{1}^{k_{1}} \mathbf{Q}_{2}^{k_{2}} \dots \mathbf{Q}_{i}^{k_{i}} \right)_{\mathbf{Q} = 1}}{1^{k_{1}} 2^{k_{2}} \dots i^{k_{i}} \cdot k_{1} \mid k_{2} \mid \dots k_{i} \mid} \\ &= \boldsymbol{\Sigma} \frac{\mathcal{F}_{q} \left( m \mid 1^{k_{1}} 2^{k_{2}} \dots i^{k_{i}} \right)}{1^{k_{1}} 2^{k_{2}} \dots i^{k_{i}} \cdot k_{1} \mid k_{2} \mid \dots k_{i} \mid} \\ &= \text{coefficient of } \boldsymbol{x}^{m} \text{ in } \boldsymbol{\Sigma} \frac{\left( 1 - \boldsymbol{x} \right)^{-k_{1}} \left( 1 - \boldsymbol{x}^{2} \right)^{-k_{2}} \dots \left( 1 - \boldsymbol{x}^{i} \right)^{-k_{i}}}{1^{k_{1}} 2^{k_{2}} \dots i^{k_{i}} \cdot k_{1} \mid k_{2} \mid \dots k_{i} \mid}; \end{split}$$

the summation being for every partition

$$k_1 + 2k_2 + \ldots + ik_i$$

of the number k.

But we know, otherwise, that the number of partitions of m, into k or fewer parts, is given by the coefficients of  $x^m$  in

$$\frac{1}{(1-x)(1-x^2)\dots(1-x^k)}.$$

Hence the identity

which being a known result supplies an interesting verification of our work. The present investigation in any case supplies one proof of it.

Art. 9. There is now no difficulty in proceeding to the result

$$\begin{split} \mathbf{D}_{m_{1}} \mathbf{D}_{m_{2}} \dots \mathbf{D}_{m_{s}} \cdot \mathbf{Q}_{1}^{k_{1}} \mathbf{Q}_{2}^{k_{2}} \dots \mathbf{Q}_{i}^{k_{s}} \\ &= \mathbf{F}_{q} \left( m_{1} \; ; \; 1^{k_{1}} 2^{k_{2}} \dots i^{k_{i}} \right) \cdot \mathbf{F}_{q} \left( m_{2} \; ; \; 1^{k_{1}} 2^{k_{2}} \dots i^{k_{i}} \right) \dots \dots \mathbf{F}_{q} \left( m_{s} \; ; \; 1^{k_{1}} 2^{k_{2}} \dots i^{k_{i}} \right) \cdot \mathbf{Q}_{1}^{k_{1}} \mathbf{Q}_{2}^{k_{2}} \dots \mathbf{Q}_{i}^{k_{i}} \; ; \end{split}$$

and the number of partitions of the multipartite number

$$m_1m_2\ldots m_s$$

into k or fewer parts, is

$$\begin{split} & D_{m_{1}}D_{m_{2}}\dots D_{m_{s}}F_{k}\left(\mathbf{Q}\right)_{\mathbf{Q}=1} \\ &= \mathbf{\Sigma}\frac{\left(D_{m_{1}}D_{m_{2}}\dots D_{m_{s}}\mathbf{Q}_{1}^{k_{1}}\mathbf{Q}_{2}^{k_{2}}\dots \mathbf{Q}_{i}^{k_{i}}\right)_{\mathbf{Q}=1}}{1^{k_{1}}2^{k_{2}}\dots i^{k_{i}}\cdot k_{1} \mid k_{2} \mid \dots k_{i} \mid} \\ &= \mathbf{\Sigma}\frac{\mathbf{F}_{q}\left(m_{1} \mid 1^{k_{1}}2^{k_{2}}\dots i^{k_{i}} \mid k_{2} \mid \dots k_{i} \mid}{1^{k_{1}}2^{k_{2}}\dots i^{k_{i}} \mid k_{2} \mid \dots k_{i} \mid} \\ &= \mathbf{\Sigma}\frac{\mathbf{F}_{q}\left(m_{1} \mid 1^{k_{1}}2^{k_{2}}\dots i^{k_{i}} \mid k_{2} \mid \dots k_{i} \mid}{1^{k_{1}}2^{k_{2}}\dots i^{k_{i}} \mid k_{2} \mid \dots k_{i} \mid} \end{split}$$

This is the general solution of the problem of enumeration in the absence of any restriction upon the magnitudes of the constituents of the multipartite parts.\*

Art. 10. It will be convenient at this point to give a few results derived from the function

$$(1-x)^{-k_1}(1-x^2)^{-k_2}\dots(1-x^i)^{-k_i}$$

which will be useful in the sequel.

$$\begin{split} \mathbf{F}_q\left(m\;;\;1^k\right) &= \binom{m+k-1}{k-1},\\ \mathbf{F}_q\left(2m\;;\;2^k\right) &= \binom{m+k-1}{k-1},\\ \mathbf{F}_q\left(im\;;\;i^k\right) &= \binom{m+k-1}{k-1},\\ \mathbf{F}_q\left(2m\;;\;12\right) &= m+1,\\ \mathbf{F}_q\left(2m\;;\;12\right) &= (m+1)^2,\\ \mathbf{F}_q\left(2m+1\;;\;12\right) &= (m+1)\left(m+2\right),\\ \mathbf{F}_q\left(2m\;;\;12^2\right) &= \binom{m+2}{2},\\ \mathbf{F}_q\left(2m+1\;;\;12^2\right) &= \binom{m+2}{2}, \end{split}$$

\* With regard to the algebraical identity met with above, the reader may compare 'Sylvester's Mathematical Papers,' vol. III., p. 598, where it is shown that for the roots of the equation

$$z^{q} - \frac{1}{1 - c}z^{q - 1} + \frac{c}{(1 - c)(1 - c^{2})}z^{q - 2} - \frac{c^{3}}{(1 - c)(1 - c^{2})(1 - c^{3})}z^{q - 3} + \dots = 0,$$

the general term being

$$(-)^n \frac{c^{\binom{n}{2}}}{(1-c)(1-c^2)\dots(1-c^n)} z^{q-n},$$

the homogeneous product-sum of order n is

$$\frac{1}{(1-c)(1-c^2)\dots(1-c^n)};$$

and the sum of the  $n^{\text{th}}$  powers of the roots is

$$\frac{1}{1-c^n}.$$

The expression of the homogeneous product-sum of order k, in terms of the sums of the powers, by the formula quoted early in this paper, gives the identity in question.

$$\begin{split} & F_q\left(3m\,;\;13\right) = F_q\left(3m+1\,;\;13\right) = F_q\left(3m+2\,;\;13\right) = m+1, \\ & F_q\left(3m\,;\;1^23\right) = \frac{1}{2}\left(m+1\right)\left(3m+2\right), \qquad F_q\left(3m+1\,;\;1^23\right) = \frac{1}{2}\left(m+1\right)\left(3m+4\right), \\ & F_q\left(3m+2\,;\;1^23\right) = \frac{1}{2}\left(m+1\right)\left(3m+6\right), \\ & F_q\left(2m\,;\;1^{k_1}2^{k_2}\right) \\ & = \binom{m+k_2-1}{k_2-1} + \binom{k_1+1}{k_1-1}\binom{m+k_2-2}{k_2-1} + \binom{k_1+3}{k_1-1}\binom{m+k_2-3}{k_2-1} + \dots + \binom{2m+k_1-1}{k_1-1}, \\ & F_q\left(2m+1\,;\;1^{k_1}2^{k_2}\right) \\ & = \binom{k_1}{k_1-1}\binom{m+k_2-1}{k_2-1} + \binom{k_1+2}{k_1-1}\binom{m+k_2-2}{k_2-1} + \dots + \binom{2m+k_1}{k_1-1}, \\ & F_q\left(3m\,;\;1^{k_1}3^{k_3}\right) \\ & = \binom{m+k_3-1}{k_3-1} + \binom{k_1+2}{k_1-1}\binom{m+k_3-2}{k_3-1} + \binom{k_1+5}{k_1-1}\binom{m+k_3-3}{k_3-1} + \dots + \binom{3m+k_1-1}{k_1-1}, \\ & F_q\left(3m+1\,;\;1^{k_1}3^{k_3}\right) \end{split}$$

$$\begin{split} \mathbf{F}_{q} \left( 3m + 2 \; ; \; 1^{k_{1}} 3^{k_{3}} \right) \\ &= \binom{k_{1} + 1}{k_{1} - 1} \binom{m + k_{3} - 1}{k_{3} - 1} + \binom{k_{1} + 4}{k_{1} - 1} \binom{m + k_{3} - 2}{k_{3} - 1} + \ldots + \binom{3m + k_{1} + 1}{k_{1} - 1} \right). \end{split}$$

 $= {k_1 \choose k_1 - 1} {m + k_3 - 1 \choose k_2 - 1} + {k_1 + 3 \choose k_1 - 1} {m + k_3 - 2 \choose k_2 - 1} + \dots + {3m + k_1 \choose k_1 - 1},$ 

The use of the Hammond operator  $D_m$  is convenient but not essential to this investigation. It is convenient from the algebraic point of view, and also because it brings into prominence properties of the operator which are in themselves important. The coefficient of  $\alpha_1^{m_1}\alpha_2^{m_2}...\alpha_s^{m_s}$  in the product  $\mathbf{Q}_1^{k_1}\mathbf{Q}_2^{k_2}...\mathbf{Q}_i^{k_i}$  is readily obtained when we remember that

$$\mathbf{Q}_{i} = \frac{1}{\left(1-\alpha^{i}\right)\left(1-\beta^{i}\right)\left(1-\gamma^{i}\right)\ldots\ldots}$$

and the various modifications are readily made for the allied functions A, B, ... U,

The Partitions of Multipartite Numbers into Two Parts.

Art. 11. The generating function which enumerates the partitions into two or fewer parts is

$$\frac{1}{2}(\mathbf{Q}_{1}^{2}+\mathbf{Q}_{2});$$

and since, from the principles just stated,

$$D_{2m}\mathbf{Q}_{1}^{2} = (2m+1)\mathbf{Q}_{1}^{2}, \qquad D_{2m+1}\mathbf{Q}_{1}^{2} = (2m+2)\mathbf{Q}_{1}^{2},$$

$$D_{2m}\mathbf{Q}_{2} = \mathbf{Q}_{2}, \qquad D_{2m+1}\mathbf{Q}_{2} = 0;$$

we find

$$\dot{\mathbf{D}}_{2m\frac{1}{2}}(\mathbf{Q}_{1}^{2}+\mathbf{Q}_{2}) = \frac{1}{2}(2m+1)\mathbf{Q}_{1}^{2}+\frac{1}{2}\mathbf{Q}_{2},$$

$$\mathbf{D}_{2m+1}\frac{1}{2}(\mathbf{Q}_{1}^{2}+\mathbf{Q}_{2}) = \frac{1}{2}(2m+2)\mathbf{Q}_{1}^{2};$$

and, by reason of the important properties possessed by the Q products in their relations with the Hammond operators, we can at once proceed to the results

$$D_{2m}^{s} = \frac{1}{2} (2m+1)^{s} \mathbf{Q}_{1}^{2} + \frac{1}{2} \mathbf{Q}_{2},$$
$$D_{2m+1}^{s} = \frac{1}{2} (2m+2)^{s} \mathbf{Q}_{1}^{2}.$$

Thence we derive, by putting  $\mathbf{Q}_1 = \mathbf{Q}_2 = 1$ , the coefficients of the symmetric functions

$$(2m^s), \qquad (2m+1^s)$$

(the exponent s meaning the numbers 2m, 2m+1 respectively s times repeated) in the development of the function  $\frac{1}{2}(\mathbf{Q}_1^2 + \mathbf{Q}_2)$ .

Thence we obtain the numbers

$$\frac{1}{2}(2m+1)^s + \frac{1}{2}, \qquad \frac{1}{2}(2m+2)^s$$

which, respectively, enumerate the ways of partitioning the multipartite numbers

$$(2m, 2m \dots \text{repeated } s \text{ times}), \qquad (2m+1, 2m+1 \dots \text{repeated } s \text{ times})$$

into two or fewer parts.

When the enumeration is concerned with exactly two parts we have clearly to subtract unity in each case. In fact the generating function is

$$\frac{1}{2}(\mathbf{Q}_{1}^{2}+\mathbf{Q}_{2})-\mathbf{Q}_{1};$$

and

$$\mathrm{D}_{2m}^s \mathbf{Q}_1 = \mathrm{D}_{2m+1}^s \mathbf{Q}_1 = \mathbf{Q}_1,$$

showing that unity must be subtracted.

The numbers then become

$$\frac{1}{2}(2m+1)^{s}-\frac{1}{2}, \qquad \frac{1}{2}(2m+2)^{s}-1.$$

These numbers also enumerate the ways of exhibiting the composite integers

$$(p_1 p_2 \dots p_s)^{2m}, (p_1 p_2 \dots p_s)^{2m+1},$$

as the product of two factors.

To obtain a general formula for the multipartite number

$$(m_1m_2 \ldots m_s)$$

we write

$$D_m \mathbf{Q}_1^2 = F_q(m; 1^2) \cdot \mathbf{Q}_1^2,$$

$$D_m \mathbf{Q}_2 = F_q(m; 2) \cdot \mathbf{Q}_2$$

then

$$D_{m_1 \overline{2}}(\mathbf{Q}_1^2 + \mathbf{Q}_2) = \frac{1}{2} \{ F_q(m_1; 1^2), \mathbf{Q}_1^2 + F_q(m_1; 2), \mathbf{Q}_2 \},$$

$$D_{m_1}D_{m_2}\frac{1}{2}\left(\mathbf{Q}_1^2+\mathbf{Q}_2\right) = \frac{1}{2}\left\{F_q\left(m_1;\ 1^2\right)F_q\left(m_2;\ 1^2\right).\mathbf{Q}_1^2+F_q\left(m_1;\ 2\right)F_q\left(m_2;\ 2\right).\mathbf{Q}_2\right\},\,$$

$$D_{m_1}D_{m_2}...D_{m_i\frac{1}{2}}(\mathbf{Q}_1^2+\mathbf{Q}_2)=\frac{1}{2}\prod_{1}^{s}F_q(m_i;1^2).\mathbf{Q}_1^2+\frac{1}{2}\prod_{1}^{s}F_q(m_i;2).\mathbf{Q}_2,$$

leading us to the number

$$rac{1}{2} \prod_{1}^{s} \mathrm{F}_{q} \left( m_{i} \; ; \; 1^{2} 
ight) + rac{1}{2} \prod_{1}^{s} \mathrm{F}_{q} \left( m_{i} \; ; \; 2 
ight),$$

as the enumerator of the partitions, into two or fewer parts, of the multipartite number

$$(m_1m_2\ldots m_s).$$

The reader will observe that the algebraic expressions of

$$F_q(m_i; 1^2)$$
 and  $F_q(m_i; 2)$ 

will depend upon the parity of  $m_i$ .

The notation has been adopted so as to save a multiplicity of formulæ in certain cases.

This of course solves the question of the factorization into two or fewer factors of the composite integer .

$$p_1^{m_1}p_2^{m_2}\dots p_s^{m_s}$$
.

We have, therefore, solved completely the question of enumerating the bipartitions of multipartite numbers.

What has been done as a question in the theory of distribution may be stated as follows. We are given an assemblage of any numerical specification and two boxes which cannot be distinguished from one another. We have found the number of ways of distributing the objects between the boxes. The similar question when the boxes are distinguished from one another is simpler and connected with the compositions of multipartite numbers.

Art. 12. At this point it may be appropriate to give a statement in regard to the nature of the solution given in this investigation.

The enumeration of the partitions of a unipartite number  $m_1$ , into k or fewer parts, is formed as a linear function of certain numbers  $a_1, b_1, c_1 \dots$ ; the linear function being

$$\lambda a_1 + \mu b_1 + \nu c_1 + \dots$$

where the numbers  $\lambda$ ,  $\mu$ ,  $\nu$ , depend only upon k.

Associated with another unipartite number  $m_2$  we have the linear function

$$\lambda a_2 + \mu b_2 + \nu c_2 + \dots$$

It has then been shown that the number of partitions, into k or fewer parts, of the multipartite number  $m_1m_2$  is

$$\lambda a_1 a_2 + \mu b_1 b_2 + \nu c_1 c_2 + \dots,$$

and in general the number of partitions, into k or fewer parts, of the multipartite number

$$m_1m_2\ldots m_s$$

is

$$\lambda a_1 a_2 \dots a_s + \mu b_1 b_2 \dots b_s + \nu c_1 c_2 \dots c_s + \dots$$

The multipartite solution is thus essentially derived from the solutions which appertain to the separate unipartite numbers whose conjunction defines the multipartite number. The numbers  $\lambda, \mu, \nu, \ldots$  are those well known in connexion with the expression of the homogeneous product sum  $h_k$  in terms of the sums of the powers  $s_1, s_2, s_3, \ldots s_k$ , the whole question is therefore reduced to finding the numbers

$$a, b, c, \dots$$

appertaining to the unipartite number m.

This, as has been shown, depends upon finding the coefficient of  $x^m$  in a function

 $(1-x)^{-k_1}(1-x^2)^{-k_2}\dots(1-x^i)^{-k_i}$ 

where

$$k_1 + k_2 + \ldots + k_i = k.$$

The possibility of the solution rests upon the remarkable circumstances that when the operator  $D_m$  is performed upon the operand

$$\mathbf{Q}_1^{k_1}\mathbf{Q}_2^{k_2}\dots\mathbf{Q}_i^{k_i}$$

its effect is to merely multiply it by an integer.

The Partitions of Multipartite Numbers into Three Parts.

Art. 13. I will, in future, merely deal with the partitions into k or fewer parts, since the result for exactly k parts is at once derived by subtracting the result for k-1 or fewer parts.

The operand is

$$\frac{1}{6} (\mathbf{Q}_1^3 + 3\mathbf{Q}_1\mathbf{Q}_2 + 2\mathbf{Q}_3),$$

and since the result depends upon the divisibility of m by both 2 and 3 it will be necessary to consider the operations of

$$D_{6m}$$
,  $D_{6m+1}$ ,  $D_{6m+2}$ ,  $D_{6m+3}$ ,  $D_{6m+4}$ ,  $D_{6m+5}$ .

The investigation is therefore in six parts.

(i.) Since

$$\begin{aligned} \mathbf{D}_{6m}\mathbf{Q}_{1}^{3} &= \begin{pmatrix} 6m+2\\2 \end{pmatrix} \mathbf{Q}_{1}^{3}, \\ \mathbf{D}_{6m}\mathbf{Q}_{1}\mathbf{Q}_{2} &= (3m+1) \mathbf{Q}_{1}\mathbf{Q}_{2}, \\ \mathbf{D}_{6m}\mathbf{Q}_{3} &= \mathbf{Q}_{3}, \end{aligned}$$

we find

$$D_{6m} \frac{1}{6} \left( \mathbf{Q}_{1}^{3} + 3\mathbf{Q}_{1}\mathbf{Q}_{2} + 2\mathbf{Q}_{3} \right) = \frac{1}{6} \left\{ \begin{pmatrix} 6m + 2 \\ 2 \end{pmatrix} \mathbf{Q}_{1}^{3} + 3 \left( 3m + 1 \right) \mathbf{Q}_{1}\mathbf{Q}_{2} + 2\mathbf{Q}_{3} \right\};$$

and immediately

$$D_{6m_1}D_{6m_2}...D_{6m_s} (\mathbf{Q}_1^3 + 3\mathbf{Q}_1\mathbf{Q}_2 + 2\mathbf{Q}_3) = \frac{1}{6} \left\{ \binom{6m_1 + 2}{2} \binom{6m_2 + 2}{2} ... \binom{6m_s + 2}{2} \mathbf{Q}_1^3 + 3(3m_1 + 1)(3m_2 + 1) ...(3m_s + 1) \mathbf{Q}_1\mathbf{Q}_2 + 2\mathbf{Q}_3 \right\};$$

and in particular

$$D_{6m}^{s} \frac{1}{6} \left( \mathbf{Q}_{1}^{3} + 3\mathbf{Q}_{1}\mathbf{Q}_{2} + 2\mathbf{Q}_{3} \right) = \frac{1}{6} \left\{ \left( \frac{6m+2}{2} \right)^{s} \mathbf{Q}_{1}^{3} + 3 \left( 3m+1 \right)^{s} \mathbf{Q}_{1}\mathbf{Q}_{2} + 2\mathbf{Q}_{3} \right\};$$

results which establish that the partitions of the multipartite number

$$6m_16m_2 \dots 6m_s$$
,

into three or fewer parts, are enumerated by

$$\frac{1}{6} \left\{ \binom{6m_1+2}{2} \left( \frac{6m_2+2}{2} \right) \dots \left( \frac{6m_s+2}{2} \right) + 3 \left( 3m_1+1 \right) \left( 3m_2+1 \right) \dots \left( 3m_s+1 \right) + 2 \right\}.$$

(ii.) Since

$$\begin{aligned} \mathbf{D}_{6m+1} \mathbf{Q}_{1}^{3} &= \binom{6m+3}{2} \mathbf{Q}_{1}^{3}, \\ \mathbf{D}_{6m+1} \mathbf{Q}_{1} \mathbf{Q}_{2} &= (3m+1) \mathbf{Q}_{1} \mathbf{Q}_{2}, \\ \mathbf{D}_{6m+1} \mathbf{Q}_{3} &= 0, \end{aligned}$$

we find

$$D_{6m+1} \frac{1}{6} \left( \mathbf{Q}_1^3 + 3 \mathbf{Q}_1 \mathbf{Q}_2 + 2 \mathbf{Q}_3 \right) = \frac{1}{6} \left\{ \binom{6m+3}{2} \cdot \mathbf{Q}_1^3 + 3 \left( 3m+1 \right) \mathbf{Q}_1 \mathbf{Q}_2 \right\};$$

and immediately

$$D_{6m_{1}+1}D_{6m_{2}+1} \dots D_{6m_{s}+1} \frac{1}{6} \left( \mathbf{Q}_{1}^{3} + 3\mathbf{Q}_{1}\mathbf{Q}_{2} + 2\mathbf{Q}_{3} \right) = \frac{1}{6} \left\{ \binom{6m_{1}+3}{2} \binom{6m_{2}+3}{2} \dots \binom{6m_{s}+3}{2} \mathbf{Q}_{1}^{3} + 3\left(3m_{1}+1\right) \left(3m_{2}+1\right) \dots \left(3m_{s}+1\right) \mathbf{Q}_{1}\mathbf{Q}_{2} \right\};$$

establishing that the partitions of the multipartite number

$$6m_1+1 6m_2+1 \dots 6m_s+1$$
,

into three or fewer parts are enumerated by

$$\frac{1}{6} \left\{ \binom{6m_1+3}{2} \binom{6m_2+3}{2} \dots \binom{6m_s+3}{2} + 3 (3m_1+1) (3m_2+1) \dots (3m_s+1) \right\}.$$
(iii.) Since 
$$D_{6m+2} \mathbf{Q}_1^{\ 3} = \binom{6m+4}{2} \mathbf{Q}_1^{\ 3},$$

$$D_{6m+2} \mathbf{Q}_1 \mathbf{Q}_2 = (3m+2) \mathbf{Q}_1 \mathbf{Q}_2,$$

$$D_{6m+2} \mathbf{Q}_3 = 0,$$

we, as above, derive, for the partitions of the multipartite number

$$6m_1+2 6m_2+2 \dots 6m_s+2$$
,

the enumerating number

$$\frac{1}{6} \left\{ \binom{6m_1+4}{2} \binom{6m_2+4}{2} \dots \binom{6m_s+4}{2} + 3 (3m_1+2) (3m_2+2) \dots (3m_s+2) \right\}.$$
(iv.) Since 
$$D_{6m+3} \mathbf{Q}_1^3 = \binom{6m+5}{2} \mathbf{Q}_1^3,$$

$$D_{6m+3} \mathbf{Q}_1 \mathbf{Q}_2 = (3m+2) \mathbf{Q}_1 \mathbf{Q}_2,$$

$$D_{6m+3} \mathbf{Q}_3 = \mathbf{Q}_3,$$

we obtain, for the multipartite number

$$6m_1 + 3 6m_2 + 3 \dots 6m_s + 3$$
,

the enumerating number

$$\frac{1}{6} \left\{ \binom{6m_1 + 5}{2} \binom{6m_2 + 5}{2} \dots \binom{6m_s + 5}{2} + 3 (3m_1 + 2) (3m_2 + 2) \dots (3m_s + 2) + 2 \right\}.$$
(v.) Also
$$D_{6m+4} \mathbf{Q}_1^3 = \binom{6m+6}{2} \mathbf{Q}_1^3,$$

$$D_{6m+4} \mathbf{Q}_1 \mathbf{Q}_2 = (3m+3) \mathbf{Q}_1 \mathbf{Q}_2,$$

$$D_{6m+4} \mathbf{Q}_3 = 0,$$

and we obtain, for the multipartite number

$$6m_1+4 6m_2+4 \dots 6m_s+4,$$

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the enumerating number

$$\frac{1}{6} \left\{ \binom{6m_1+6}{2} \binom{6m_2+6}{2} \dots \binom{6m_s+6}{2} + 3(3m_1+3)(3m_2+3) \dots (3m_s+3) \right\}.$$

(vi.) Lastly, since

$$\mathbf{D}_{6m+5}\mathbf{Q}_{1}^{3} = \begin{pmatrix} 6m+7\\2 \end{pmatrix} \mathbf{Q}_{1}^{3},$$
  $\mathbf{D}_{6m+5}\mathbf{Q}_{1}\mathbf{Q}_{2} = (3m+3)\mathbf{Q}_{1}\mathbf{Q}_{2},$   $\mathbf{D}_{6m+5}\mathbf{Q}_{3} = 0,$ 

we obtain, for the multipartite number

$$6m_1+5$$
  $6m_2+5$  ...  $6m_s+5$ ,

the enumerating number

$$\frac{1}{6} \left\{ \binom{6m_1+7}{2} \binom{6m_2+7}{2} \dots \binom{6m_s+7}{2} + 3(3m_1+3)(3m_2+3) \dots (3m_s+3) \right\}.$$

Finally, in the notation employed for the bipartite case, for the multipartite number

$$m_1 m_2 \dots m_s$$

we have the enumerating number

$$\frac{1}{6} \left\{ \prod_{1}^{s} F_{q}(m_{i}; 1^{3}) + 3 \prod_{1}^{s} F_{q}(m_{i}; 1, 2) + 2 \prod_{1}^{s} F_{q}(m_{i}; 3) \right\}.$$

#### Art. 14. I collect these results:—

Multipartite Numbers. Number of Partitions into three or fewer parts.  $6m \ 6m \ 6m \ repeated \ s \ times \qquad \frac{1}{3!} \left\{ \begin{pmatrix} 6m+2 \\ 2 \end{pmatrix}^s + 3 \ (3m+1)^s + 2 \right\} \ .$   $6m+1 \ 6m+1 \ 6m+1 \ repeated \ s \ times \qquad \frac{1}{3!} \left\{ \begin{pmatrix} 6m+3 \\ 2 \end{pmatrix}^s + 3 \ (3m+1)^s \right\}$   $6m+2 \ 6m+2 \ 6m+2 \qquad , \qquad , \qquad \frac{1}{3!} \left\{ \begin{pmatrix} 6m+4 \\ 2 \end{pmatrix}^s + 3 \ (3m+2)^s \right\}$   $6m+3 \ 6m+3 \ 6m+3 \qquad , \qquad , \qquad \frac{1}{3!} \left\{ \begin{pmatrix} 6m+5 \\ 2 \end{pmatrix}^s + 3 \ (3m+2)^s + 2 \right\}$   $6m+4 \ 6m+4 \ 6m+4 \qquad , \qquad , \qquad \frac{1}{3!} \left\{ \begin{pmatrix} 6m+6 \\ 2 \end{pmatrix}^s + 3 \ (3m+3)^s \right\}$   $6m+5 \ 6m+5 \ 6m+5 \qquad , \qquad , \qquad \frac{1}{3!} \left\{ \begin{pmatrix} 6m+7 \\ 2 \end{pmatrix}^s + 3 \ (3m+3)^s \right\}.$ 

Multipartite Numbers.

Number of Partitions into exactly three parts.

$$\frac{1}{3!} \left\{ \begin{pmatrix} 6m+2 \\ 2 \end{pmatrix}^s + 3(3m+1)^s - 3(6m+1)^s - 1 \right\}$$

$$6m+1 \ 6m+1 \ 6m+1 \ repeated s \ times \qquad \frac{1}{3!} \left\{ \begin{pmatrix} 6m+3 \\ 2 \end{pmatrix}^s + 3(3m+1)^s - 3(6m+2)^s \right\}$$

$$6m+2 \ 6m+2 \ 6m+2 \qquad , \qquad , \qquad \frac{1}{3!} \left\{ \begin{pmatrix} 6m+4 \\ 2 \end{pmatrix}^s + 3(3m+2)^s - 3(6m+3)^s - 3 \right\}$$

$$6m+3 \ 6m+3 \ 6m+3 \qquad , \qquad , \qquad \frac{1}{3!} \left\{ \begin{pmatrix} 6m+5 \\ 2 \end{pmatrix}^s + 3(3m+2)^s - 3(6m+4)^s + 2 \right\}$$

$$6m+4 \ 6m+4 \ 6m+4 \qquad , \qquad , \qquad \frac{1}{3!} \left\{ \begin{pmatrix} 6m+6 \\ 2 \end{pmatrix}^s + 3(3m+3)^s - 3(6m+5)^s - 3 \right\}$$

$$6m+5 \ 6m+5 \ 6m+5 \qquad , \qquad , \qquad \frac{1}{3!} \left\{ \begin{pmatrix} 6m+6 \\ 2 \end{pmatrix}^s + 3(3m+3)^s - 3(6m+6)^s - 3 \right\}$$

As a verification, connected with unipartite partitions, we put s=1 in these last six formulæ, and reach the six numbers

$$3m^2$$
,  $3m^2+m$ ,  $3m^2+2m$ ,  $3m^2+3m+1$ ,  $3m^2+4m+1$ ,  $3m^2+5m+2$ ,

and since these may be exhibited in the forms

$$\frac{(6m)^2}{12}, \quad \frac{(6m+1)^2}{12} - \frac{1}{12}, \quad \frac{(6m+2)^2}{12} - \frac{1}{3}, \quad \frac{(6m+3)^2}{12} + \frac{1}{4}, \quad \frac{(6m+4)^2}{12} - \frac{1}{3}, \quad \frac{(6m+5)^2}{12} - \frac{1}{12},$$

we verify the well-known theorem which states that the number of tripartitions of n is the nearest integer to  $\frac{n^2}{12}$ .

The Partitions of Multipartite Numbers into Four Parts.

Art. 15. The operand is

$$\frac{1}{2.4} \left( \mathbf{Q}_{1}^{4} + 6\mathbf{Q}_{1}^{2}\mathbf{Q}_{2} + 3\mathbf{Q}_{2}^{2} + 8\mathbf{Q}_{1}\mathbf{Q}_{3} + 6\mathbf{Q}_{4} \right)$$

since the result depends upon the divisibility of m by the numbers 2, 3 and 4, and 12 is the least common multiple of those numbers, it will be necessary to take the operator suffix to the modulus 12, and the investigation is, therefore, in twelve parts.

We have 
$$D_{m}\mathbf{Q}_{1}^{4} = \binom{m+3}{3}\mathbf{Q}_{1}^{4},$$

$$D_{2m}\mathbf{Q}_{1}^{2}\mathbf{Q}_{2} = (m+1)^{2}\mathbf{Q}_{1}^{2}\mathbf{Q}_{2},$$

$$D_{2m+1}\mathbf{Q}_{1}^{2}\mathbf{Q}_{2} = (m+1)(m+2)\mathbf{Q}_{1}^{2}\mathbf{Q}_{2},$$

$$D_{2m}\mathbf{Q}_{2}^{2} = (m+1)\mathbf{Q}_{2}^{2},$$

$$D_{2m+1}\mathbf{Q}_{2}^{2} = 0,$$

$$D_{3m}\mathbf{Q}_{1}\mathbf{Q}_{3} = (m+1)\mathbf{Q}_{1}\mathbf{Q}_{3},$$

$$D_{3m+1}\mathbf{Q}_{1}\mathbf{Q}_{3} = (m+1)\mathbf{Q}_{1}\mathbf{Q}_{3},$$

$$D_{3m+2}\mathbf{Q}_{1}\mathbf{Q}_{3} = (m+1)\mathbf{Q}_{1}\mathbf{Q}_{3},$$

$$D_{4m}\mathbf{Q}_{4} = \mathbf{Q}_{4},$$

$$D_{4m}\mathbf{Q}_{4} = \mathbf{Q}_{4},$$

$$D_{4m+1}\mathbf{Q}_{4} = D_{4m+2}\mathbf{Q}_{4} = D_{4m+3}\mathbf{Q}_{4} = 0.$$

Utilising these results and taking as operators  $D^{s}_{12m}$ ,  $D^{s}_{12m+1}$ , ...  $D^{s}_{12m+11}$  in succession we find for partitions into four or fewer parts:—

Multipartite Numbers. Number of Partitions into four or fewer parts.  $\frac{1}{4!} \left\{ \left( \frac{12m+3}{3} \right)^s + 6 (6m+1)^{2s} + 3 (6m+1)^s + 8 (4m+1)^s + 6 \right\}$  $12m \ 12m \ 12m \ repeated s \ times$ 12m+1 12m+1 12m+1 repeated s times  $\frac{1}{4!}\left\{ \begin{pmatrix} 12m+4 \\ 3 \end{pmatrix}^s + 12 \begin{pmatrix} 6m+2 \\ 2 \end{pmatrix}^s \right\}$  $+8(4m+1)^{s}$ ","  $\frac{1}{4!} \left\{ \left( \frac{12m+5}{3} \right)^s + 6(6m+2)^{2s} + 3(6m+2)^s + 8(4m+1)^s \right\}$ 12m+2 12m+2 12m+2 $\frac{1}{4!} \left\{ \left( \frac{12m+6}{3} \right)^s + 12 \left( \frac{6m+3}{2} \right)^s \right\}$  $+8(4m+2)^{s}$ 12m+3 12m+3 12m+3","  $\frac{1}{4!} \left\{ \left( \frac{12m+7}{3} \right)^s + 6 (6m+3)^{2s} + 3 (6m+3)^s + 8 (4m+2)^s + 6 \right\}$ 12m+4 12m+4 12m+4 $\frac{1}{4!} \left\{ \left( \frac{12m+8}{3} \right)^s + 12 \left( \frac{6m+4}{2} \right)^s \right\}$  $+8(4m+2)^{s}$ 12m+5 12m+5 12m+5","  $\frac{1}{4!} \left\{ \left( \frac{12m+9}{3} \right)^s + 6(6m+4)^{2s} + 3(6m+4)^s + 8(4m+3)^s \right\}$ 12m+6 12m+6 12m+6 $\frac{1}{4!} \left\{ \left( \frac{12m+10}{3} \right)^s + 12 \left( \frac{6m+5}{2} \right)^s \right\}$  $+8(4m+3)^{s}$ 12m+7 12m+7 12m+7"," ","  $\frac{1}{4!} \left\{ \left( \frac{12m+11}{3} \right)^s + 6 \left( 6m+5 \right)^{2s} + 3 \left( 6m+5 \right)^s + 8 \left( 4m+3 \right)^s + 6 \right\}$ 12m+8 12m+8 12m+8 $\frac{1}{4!}\left\{\left(\frac{12m+12}{3}\right)^s+12\left(\frac{6m+6}{2}\right)^s\right\}$  $+8(4m+4)^{s}$ 12m+9 12m+9 12m+9","  $\frac{1}{4!} \left\{ \left( \frac{12m+13}{3} \right)^s + 6(6m+6)^{2s} + 3(6m+6)^s + 8(4m+4)^s \right\}$ 12m+10 12m+10 12m+10 $\frac{1}{4!}\left\{ \left(\frac{12m+14}{3}\right)^{s}+12\left(\frac{6m+7}{2}\right)^{s} \right\}$  $+8(4m+4)^{s}$ 12m+11 12m+11 12m+11

For the unipartite case we put s = 1 and find, reading by rows, the numbers

$m^3$ .	$m^2$ ,	m.	1.		
12 12	15 18	6 8	1		
12 12 12	$\begin{array}{c} 21 \\ 24 \end{array}$	12 15	$\frac{2}{3}$		
$egin{array}{c} 12 \\ 12 \\ 12 \end{array}$	27 30 33	20 24 30	5 6 9		
12 12	36 39	35 42	11 15		
$ \begin{array}{c c} 12 \\ 12 \\ 12 \end{array} $	42 45 48	48 56 63	$egin{array}{c} 18 \\ 23 \\ 27 \end{array}$		
12	10	00	<i>u</i> •		

which admit of easy verification.

In the notation of this paper, for the multipartite number

$$m_1m_2 \ldots m_s$$
,

we have the enumerating number

$$\frac{1}{24} \left\{ \prod_{i=1}^{s} F_q(m_i; 1^4) + 6 \prod_{i=1}^{s} F_q(m_i; 1^22) + 3 \prod_{i=1}^{s} F_q(m_i; 2^2) + 8 \prod_{i=1}^{s} F_q(m_i; 13) + 6 \prod_{i=1}^{s} F_q(m_i; 4) \right\}.$$

#### SECTION II.

Art. 16. The multipartite partitions which have been under consideration above have involved multipartite parts, and the integers which are constituents of those parts have been quite unrestricted in magnitude. We have now to consider the enumeration when these magnitudes are subject to various restrictions.

The first restriction to come before us is that in which no integer constituent of a multipartite partition is to exceed unity.

We form a fraction  $\mathbf{A}_1$  from  $\mathbf{Q}_1$  by striking out from the latter every partition which involves a part greater than unity.

Thus

$$\mathbf{A}_1 = 1 + (1) + (1^2) + (1^3) + \dots$$
 ad inf.

We now form  $\mathbf{A}_2$ ,  $\mathbf{A}_3$ , ...  $\mathbf{A}_i$ , ..., from  $\mathbf{A}_1$ , by doubling, trebling, ... multiplying by i, ... all the bracket numbers of  $\mathbf{A}_1$ , in the same way as we formed  $\mathbf{Q}_2$ ,  $\mathbf{Q}_3$ , ...  $\mathbf{Q}_i$ , ... from  $\mathbf{Q}_1$ .

Thus

We proceed in this manner because we desire the development of the generating symmetric function

$$\frac{1}{(1-\alpha)(1-\alpha\alpha)(1-\beta\alpha)\dots(1-\alpha\beta\alpha)(1-\alpha\gamma\alpha)\dots(1-\alpha\beta\gamma\alpha)\dots(1-\alpha\beta\gamma\delta\alpha)\dots}$$

there being a denominator factor for every  $\alpha$ ,  $\beta$ ,  $\gamma$ , ... product in which no letter is repeated. The expansion of this fraction involves the whole of the homogeneous product-sums of such  $\alpha$ ,  $\beta$ ,  $\gamma$ , ... products; and we form these product-sums through the medium of the sums of the powers of the products which are, in fact,  $\mathbf{A}_1$ ,  $\mathbf{A}_2$ , ...  $\mathbf{A}_i$ , .... The development is

$$1 + a\mathbf{A}_{1}$$

$$+ \frac{a^{2}}{2!}(\mathbf{A}_{1}^{2} + \mathbf{A}_{2})$$

$$+ \frac{a^{3}}{3!}(\mathbf{A}_{1}^{3} + 3\mathbf{A}_{1}\mathbf{A}_{2} + 2\mathbf{A}_{3})$$

$$+ \dots$$

$$+ a^{k} \mathbf{F}_{k}(\mathbf{A})$$

$$+ \dots$$

where

$$\mathbf{F}_{k}(\mathbf{A}) = \mathbf{\Sigma} \frac{\mathbf{A}_{1}^{k_{1}} \mathbf{A}_{2}^{k_{2}} \dots \mathbf{A}_{i}^{k_{i}}}{1^{k_{1}} 2^{k_{2}} \dots i^{k_{i}} \cdot k_{1} \mid k_{2} \mid k_{i}}!,$$

precisely similar to the Q development with A written for Q.

It may at this point be worth stating that the two developments may be written

$$\exp\left(a\mathbf{Q}_{1}+\frac{1}{2}a^{2}\mathbf{Q}_{2}+\frac{1}{3}a^{3}\mathbf{Q}_{3}+\ldots\right),\qquad \exp\left(a\mathbf{A}_{1}+\frac{1}{2}a^{2}\mathbf{A}_{2}+\frac{1}{3}a^{3}\mathbf{A}_{3}+\ldots\right)$$

respectively.

We now examine the effect of the Hammond operators upon this infinite set of A functions. It is clear from the well-known fundamental property of the operators that

$$D_i \mathbf{A}_i = \mathbf{A}_i$$

and

$$D_m \mathbf{A}_i = 0 \quad \text{when} \quad m \neq i,$$

results of great simplicity.

When  $D_m$  operates upon any product

$$\mathbf{A}_1^{k_1}\mathbf{A}_2^{k_2}\ldots\mathbf{A}_i^{k_i}$$

the demonstration proceeds as with the Q function ante.

Writing out the A product at length and underneath it any composition of m into  $k_1+k_2+\ldots+k_i$  parts, zero counting as a part, we note that if the composition operator is to have the effect of multiplying the product by unity and not by zero, every part under the first  $k_1$  factors of the operand must be zero or unity; every part under the next  $k_2$  factors must be zero or 2; every part under the next  $k_3$  factors must be zero or 3; and so on, until finally every part under the last  $k_i$  factors must be zero or i.

The number of compositions of m which possess these properties is equal to the coefficients of  $x^m$  in the developments of

$$(1+x)^{k_1}(1+x^2)^{k_2}(1+x^3)^{k_3}\dots(1+x^i)^{k_i}$$

which may be written

$$\left(\frac{1-x^2}{1-x}\right)^{k_1} \left(\frac{1-x^4}{1-x^2}\right)^{k_2} \left(\frac{1-x^6}{1-x^3}\right)^{k_3} \dots \left(\frac{1-x^{2i}}{1-x^i}\right)^{k_i},$$

or, in Cayley's notation,

$$\frac{(2)^{k_1}(4)^{k_2}(6)^{k_3}\dots(2i)^{k_i}}{(1)^{k_1}(2)^{k_2}(3)^{k_3}\dots(i)^{k_i}}\cdot$$

Let this coefficient be denoted by

$$F_a(m; 1^{k_1}2^{k_2}\dots i^{k_i})$$

so that

$$\mathrm{D}_{m}\mathbf{A}_{1}{}^{k_{1}}\mathbf{A}_{2}{}^{k_{2}}\ldots \mathbf{A}_{i}{}^{k_{i}} = \mathrm{F}_{a}(m\,;\,1^{k_{1}}2^{k_{2}}\ldots\,i^{k_{i}})\,\mathbf{A}_{1}{}^{k_{1}}\mathbf{A}_{2}{}^{k_{2}}\ldots \mathbf{A}_{i}{}^{k_{i}}.$$

Looking to the symmetric function expressions of  $\mathbf{A}_1$ ,  $\mathbf{A}_2$ ...  $\mathbf{A}_i$ ..., it will be noted that the only portion of the product

$$\mathbf{A}_1^{k_1}\mathbf{A}_2^{k_2}\ldots \mathbf{A}_i^{k_i},$$

that is free from the elements  $\alpha$ ,  $\beta$ ,  $\gamma$ ..., is unity.

Hence the portion of

$$D_m \mathbf{A}_1^{k_1} \mathbf{A}_2^{k_2} \dots \mathbf{A}_i^{k_i}$$

that is free from the elements, is

$$F_a(m; 1^{k_1}2^{k_2}...i^{k_i});$$

and we may write, as before,

$$(D_m \mathbf{A}_1^{k_1} \mathbf{A}_2^{k_2} \dots \mathbf{A}_i^{k_i})_{\mathbf{A}=1} = F_a(m; 1^{k_1} 2^{k_2} \dots i^{k_i}).$$

The number of partitions of the unipartite number m into k or fewer parts, restricted not to exceed unity, is therefore

$$\begin{split} \mathrm{D}_{m}\mathrm{F}_{k}(\mathbf{A})_{\mathbf{A}=1} &= \boldsymbol{\Sigma} \frac{\left(\mathrm{D}_{m}\mathbf{A}_{1}^{k_{1}}\mathbf{A}_{2}^{k_{2}}\ldots\mathbf{A}_{i}^{k_{i}}\right)_{\mathbf{A}=1}}{1^{k_{1}}2^{k_{2}}\ldots i^{k_{i}} \cdot k_{1} ! \ k_{2} ! \ldots k_{i} !}\,, \\ &= \boldsymbol{\Sigma} \frac{\mathrm{F}_{a}\left(m \ ; \ 1^{k_{1}}2^{k_{2}}\ldots i^{k_{i}}\right)}{1^{k_{1}}2^{k_{2}}\ldots i^{k_{i}} \cdot k_{1} ! \ k_{2} ! \ldots k_{i} !}, \\ &= \mathrm{coefficients} \ \mathrm{of} \ x^{m} \ \mathrm{in} \\ &= \boldsymbol{\Sigma} \frac{\left(\frac{1-x^{2}}{1-x}\right)^{k_{1}}\left(\frac{1-x^{4}}{1-x^{2}}\right)^{k_{2}}\ldots\left(\frac{1-x^{2i}}{1-x^{i}}\right)^{k_{i}}}{1^{k_{1}}2^{k_{2}}\ldots i^{k_{i}} \cdot k_{1} ! \ k_{2} ! \ldots k_{i} !}, \end{split}$$

the summation being for every partition

$$k_1 + 2k_2 + \ldots + ik_i$$

of the number k.

Now, obviously, the number we seek is also the coefficient of  $x^m$  in  $1+x+x^2+\ldots+x^k$ . Hence the formula

when k is 3 the identity is

$$\frac{1}{6} \left\{ (1+x)^3 + 3(1+x)(1+x^2) + 2(1+x^3) \right\} = 1 + x + x^2 + x^3.$$

We have now the result

$$D_{m_1}D_{m_2}...D_{m_s}.\mathbf{A}_1^{k_1}\mathbf{A}_2^{k_2}...\mathbf{A}_i^{k_i}$$

$$= F_{\sigma}(m_1; 1^{k_1}2^{k_2}...i^{k_i}).F_{\sigma}(m_2; 1^{k_1}2^{k_2}...i^{k_i})...F(m_s; 1^{k_1}2^{k_2}...i^{k_i}).\mathbf{A}_1^{k_1}\mathbf{A}_2^{k_2}...\mathbf{A}_i^{k_i};$$

and the number of partitions of the multipartite number

$$m_1 m_2 \dots m_s$$

into k or fewer parts, no integer constituent of the multipartite parts exceeding unity, is

$$\geq \frac{F_a(m_1; 1^{k_1}2^{k_2}\dots i^{k_i}) \cdot F_a(m_2; 1^{k_1}2^{k_2}\dots i^{k_i}) \dots F_a(m_s; 1^{k_1}2^{k_1}\dots i^{k_i})}{1^{k_1}2^{k_2}\dots i^{k_i} \cdot k_1! |k_2!\dots k_i|!};$$

the general solution of the problem.

Some examples are now given.

For the partitions into two, or fewer parts, it is only necessary to consider the cases m = 1 and m = 2, since there are no partitions of the nature examined when m > 2.

$$D_{1}^{s_{1}} \frac{1}{2} (\mathbf{A}_{1}^{2} + \mathbf{A}_{2}) = \frac{1}{2} \cdot 2^{s_{1}} \mathbf{A}_{1}^{2},$$
  
$$D_{2}^{s_{2}} \frac{1}{2} (\mathbf{A}_{1}^{2} + \mathbf{A}_{2}) = \frac{1}{2} (\mathbf{A}_{1}^{2} + \mathbf{A}_{2}),$$

so that

$$D_{1} \frac{1}{2} (\mathbf{A}_{1}^{2} + \mathbf{A}_{2}) = \frac{1}{2} \cdot 2\mathbf{A}_{1}^{2},$$

$$D_{2} \frac{1}{2} (\mathbf{A}_{1}^{2} + \mathbf{A}_{2}) = \frac{1}{2} (\mathbf{A}_{1}^{2} + \mathbf{A}_{2}),$$

and

$$D_1^{s_1}D_2^{s_2}\frac{1}{2}(\mathbf{A}_1^2+\mathbf{A}_2)=\frac{1}{2}\cdot 2^{s_1}\mathbf{A}_1^2$$

results which show

(i.) that the multipartite number

111 ...  $s_1$  times repeated,

has  $2^{s_1-1}$  partitions into two or fewer parts;

(ii.) that the number

 $222 \dots s_2$  times repeated,

has one partition into two or fewer parts;

(iii.) that the multipartite number

$$222 \dots s_2$$
 times,  $111 \dots s_1$  times,

has 2<sup>s<sub>1</sub>-1</sup> partitions into two or fewer parts.

Ex. gr. the multipartite number 2111 has the four partitions

$$(1111 1000), (1011 1100), (1101 1010), (1110 1001).$$

For the partitions, into three or fewer parts, we have

$$\begin{aligned} &D_{3} \frac{1}{6} \left( \mathbf{A}_{1}^{3} + 3\mathbf{A}_{1}\mathbf{A}_{2} + 2\mathbf{A}_{3} \right) = \frac{1}{6} \left( \mathbf{A}_{1}^{3} + 3\mathbf{A}_{1}\mathbf{A}_{2} + 2\mathbf{A}_{3} \right), \\ &D_{2} \frac{1}{6} \left( \mathbf{A}_{1}^{3} + 3\mathbf{A}_{1}\mathbf{A}_{2} + 2\mathbf{A}_{3} \right) = \frac{1}{6} \left( 3\mathbf{A}_{1}^{3} + 3\mathbf{A}_{1}\mathbf{A}_{2} \right), \\ &D_{1} \frac{1}{6} \left( \mathbf{A}_{1}^{3} + 3\mathbf{A}_{1}\mathbf{A}_{2} + 2\mathbf{A}_{3} \right) = \frac{1}{6} \left( 3\mathbf{A}_{1}^{3} + 3\mathbf{A}_{1}\mathbf{A}_{2} \right), \end{aligned}$$

to which we may add for symmetry

we gather that

$$\begin{split} D_{0}\frac{1}{6}\left(\mathbf{A}_{1}^{3}+3\mathbf{A}_{1}\mathbf{A}_{2}+2\mathbf{A}_{3}\right)&=\frac{1}{6}\left(\mathbf{A}_{1}^{3}+3\mathbf{A}_{1}\mathbf{A}_{2}+2\mathbf{A}_{3}\right);\\ D_{3}^{s_{3}}\frac{1}{6}\left(\mathbf{A}_{1}^{3}+3\mathbf{A}_{1}\mathbf{A}_{2}+2\mathbf{A}_{3}\right)&=\frac{1}{6}\left(\mathbf{A}_{1}^{3}+3\mathbf{A}_{1}\mathbf{A}_{2}+2\mathbf{A}_{3}\right),\\ D_{2}^{s_{2}}\frac{1}{6}\left(\mathbf{A}_{1}^{3}+3\mathbf{A}_{1}\mathbf{A}_{2}+2\mathbf{A}_{3}\right)&=\frac{1}{6}\left(3^{s_{2}}\mathbf{A}_{1}^{3}+3\mathbf{A}_{1}\mathbf{A}_{2}\right),\\ D_{1}^{s_{1}}\frac{1}{6}\left(\mathbf{A}_{1}^{3}+2\mathbf{A}_{1}\mathbf{A}_{2}+2\mathbf{A}_{3}\right)&=\frac{1}{6}\left(3^{s_{1}}\mathbf{A}_{1}^{3}+3\mathbf{A}_{1}\mathbf{A}_{2}\right),\\ D_{3}^{s_{3}}\dot{D}_{2}^{s_{2}}D_{1}^{s_{1}}\frac{1}{6}\left(\mathbf{A}_{1}^{3}+3\mathbf{A}_{1}\mathbf{A}_{2}+2\mathbf{A}_{3}\right)&=\frac{1}{6}\left(3^{s_{1}+s_{2}}\mathbf{A}_{1}^{3}+3\mathbf{A}_{1}\mathbf{A}_{2}\right); \end{split}$$

and it follows that the multipartite number

$$333 \dots s_3$$
 times,  $222 \dots s_2$  times,  $111 \dots s_1$  times,

has  $\frac{1}{6}(3^{s_1+s_2}+3)$  partitions, into three or fewer parts, of the nature we are considering. Vol. CCXVII.—A.

Ex. gr. The multipartite number 3221 has the five partitions

Art. 17. Again, to pass to a different restriction, if no integer constituent of a multipartite part is to exceed 2, we strike out from the **Q** functions all partitions which involve integers greater than 2 and arrive at an infinite set of **B** functions which can be dealt with in a similar way. Thus

$$\mathbf{B}_{1} = 1 + (1) + (2) + (1^{2}) + (21) + (1^{3}) + (2^{2}) + (21^{2}) + (1^{4}) + \dots \quad \text{ad inf.}$$

$$\mathbf{B}_{2} = 1 + (2) + (4) + (2^{2}) + (42) + (2^{3}) + (4^{2}) + (42^{2}) + (2^{4}) + \dots \quad , \quad , \quad ,$$

$$\mathbf{B}_{i} = 1 + (i) + (2i) + (i^{2}) + (2i, i) + (i^{3}) + (2i, 2i) + (2i, i, i) + (i^{4}) + \dots \quad , \quad , \quad ,$$

In regard to the Hammond operators

$$D_i \mathbf{B}_i = D_{ij} \mathbf{B}_j = \mathbf{B}_i;$$

while every other operator causes  $\mathbf{B}_i$  to vanish.

To find the effect of  $D_m$  upon the product

$$\mathbf{B}_{\!\scriptscriptstyle 1}{}^{k_1}\!\mathbf{B}_{\!\scriptscriptstyle 2}{}^{k_2}\,\ldots\,\mathbf{B}_{\!\scriptscriptstyle i}{}^{k_i}$$

we observe that  $D_m$  operates through the compositions of m into exactly  $k_1 + k_2 + \ldots + k_i$  parts, zero counting as a part. In order that a particular composition operator shall not cause the product to vanish, the  $k_s$  factors of  $\mathbf{B}_s^{k_s}$  must only be operated upon by  $D_0(\equiv 1)$ ,  $D_s$  and  $D_{2s}$ . Hence the number of compositions which multiply the product by unity and not by zero is given by the coefficient of  $x^m$  in the development of

which is  $\frac{(1+x+x^2)^{k_1} \left(1+x^2+x^4\right)^{k_2} \dots \left(1+x^i+x^{2i}\right)^{k_i}}{\left(\frac{1-x^3}{1-x}\right)^{k_1} \left(\frac{1-x^6}{1-x^2}\right)^{k_2} \dots \left(\frac{1-x^{3i}}{1-x^i}\right)^{k_i}}.$ 

This establishes that the effect of  $D_m$  upon the product is to multiply it by this coefficient.

The generating function is

$$1 + a\mathbf{B}_{1} + \frac{a^{2}}{2!}(\mathbf{B}_{1}^{2} + \mathbf{B}_{2}) + \frac{a^{3}}{3!}(\mathbf{B}_{1}^{3} + 3\mathbf{B}_{1}\mathbf{B}_{2} + 2\mathbf{B}_{3}) + \dots + a^{k}\mathbf{F}_{k}(\mathbf{B}) + \dots$$

where

$$\mathbf{F}_{k}(\mathbf{B}) = \mathbf{\Sigma} rac{\mathbf{B}_{1}^{-k_{1}} \mathbf{B}_{2}^{-k_{2}} \dots \mathbf{B}_{i}^{-k_{i}}}{1^{k_{1}} 2^{k_{2}} \dots i^{k_{i}} \cdot k_{1} ! \ k_{2} ! \dots k_{i} !}$$

Thence we find

$$\begin{split} (\mathbf{D}_{m_1} \mathbf{D}_{m_2} \dots \mathbf{D}_{m_s} \mathbf{F}_{k} (\mathbf{B}))_{\mathbf{B} = 1} \\ &= \sum \frac{\mathbf{F}_{b} (m_1 \; ; \; 1^{k_1} 2^{k_2} \dots i^{k_i}) \; . \; \mathbf{F}_{b} (m_2 \; ; \; 1^{k_1} 2^{k_2} \dots i^{k_i}) \; ... \; \mathbf{F} (m_s \; ; \; 1^{k_1} 2^{k_2} \dots i^{k_i})}{1^{k_1} 2^{k_2} \dots i^{k_i} \; ... \; i^{k_i} \; ... \; k_s \; !} \; ; \end{split}$$

the solution of the problem of enumeration in respect of the multipartite number  $m_1m_2 \dots m_s$ .

If, in the function  $F_k(\mathbf{B})$ , we substitute

$$\frac{1-x^{3s}}{1-x^s}$$
for  $\mathbf{B}_s$ ,

we obtain

$$\frac{\left(1-x^{k+1}\right)\left(1-x^{k+2}\right)}{\left(1-x\right)\left(1-x^2\right)},$$

because this function enumerates unipartite partitions whose parts are limited in number by k and in magnitude by 2.

As an example consider partitions into three parts. We have the symmetrical results

$$\begin{split} &D_{6} \frac{1}{6} \left( \mathbf{B}_{1}^{3} + 3 \mathbf{B}_{1} \mathbf{B}_{2} + 2 \mathbf{B}_{3} \right) = \frac{1}{6} \left( \mathbf{B}_{1}^{3} + 3 \mathbf{B}_{1} \mathbf{B}_{2} + 2 \mathbf{B}_{3} \right), \\ &D_{5} \frac{1}{6} \left( \mathbf{B}_{1}^{3} + 3 \mathbf{B}_{1} \mathbf{B}_{2} + 2 \mathbf{B}_{3} \right) = \frac{1}{6} \left( 3 \mathbf{B}_{1}^{3} + 3 \mathbf{B}_{1} \mathbf{B}_{2} \right), \\ &D_{4} \frac{1}{6} \left( \mathbf{B}_{1}^{3} + 3 \mathbf{B}_{1} \mathbf{B}_{2} + 2 \mathbf{B}_{3} \right) = \frac{1}{6} \left( 6 \mathbf{B}_{1}^{3} + 3 \cdot 2 \mathbf{B}_{1} \mathbf{B}_{2} \right), \\ &D_{3} \frac{1}{6} \left( \mathbf{B}_{1}^{3} + 3 \mathbf{B}_{1} \mathbf{B}_{2} + 2 \mathbf{B}_{3} \right) = \frac{1}{6} \left( 7 \mathbf{B}_{1}^{3} + 3 \mathbf{B}_{1} \mathbf{B}_{2} + 2 \mathbf{B}_{3} \right), \end{split}$$

and D<sub>2</sub>, D<sub>1</sub>, D<sub>0</sub>, yield the same results as D<sub>4</sub>, D<sub>5</sub>, D<sub>6</sub>, respectively.

The number m, not exceeding 6,  $D_m$  and  $D_{6-m}$  produce upon the operand the same result. This symmetry naturally follows from the known property of the function

$$\frac{(1-x^{k+1})(1-x^{k+2})}{(1-x)(1-x^2)}$$

which on expansion is, as regards coefficients, centrally symmetrical.

We now at once deduce that

$$D_{6}^{s}F_{3}(\mathbf{B}) = D_{0}^{s}F_{3}(\mathbf{B}) = \frac{1}{6} (\mathbf{B}_{1}^{3} + 3\mathbf{B}_{1}\mathbf{B}_{2} + 2\mathbf{B}_{3})$$

$$D_{5}^{s}F_{3}(\mathbf{B}) = D_{1}^{s}F_{3}(\mathbf{B}) = \frac{1}{6} (3^{s}\mathbf{B}_{1}^{3} + 3\mathbf{B}_{1}\mathbf{B}_{2})$$

$$D_{4}^{s}F_{3}(\mathbf{B}) = D_{2}^{s}F_{3}(\mathbf{B}) = \frac{1}{6} (6^{s}\mathbf{B}_{1}^{3} + 3 \cdot 2^{s}\mathbf{B}_{1}\mathbf{B}_{2})$$

$$D_{3}^{s}F_{3}(\mathbf{B}) = \frac{1}{6} (7^{s}\mathbf{B}_{1}^{s} + 3\mathbf{B}_{1}\mathbf{B}_{2} + 2\mathbf{B}_{3}).$$

$$O_{3}^{s}F_{3}(\mathbf{B}) = \frac{1}{6} (7^{s}\mathbf{B}_{1}^{s} + 3\mathbf{B}_{1}\mathbf{B}_{2} + 2\mathbf{B}_{3}).$$

We deduce that the multipartite number

has only one partition of the nature we consider, and this of course is quite obvious.

That the multipartite numbers

555 ... s times, 111 ... s times

have each of them

 $\frac{1}{6}(3^s+3)$  partitions;

the multipartite numbers

444 ... s times, 222 ... s times,

have each of them

 $\frac{1}{6}(6^s+3\cdot 2^s)$  partitions;

and the number

 $333 \dots s \text{ times}$ 

 $\frac{1}{6}(7^s+5)$  partitions.

Also the multipartite number

 $333 \dots s$  times,  $222 \dots t$  times

has

$$\frac{1}{6} \left( 7^s \cdot 6^t + 3 \cdot 2^s \right)$$

partitions, and various other results.

The symmetry shown above in the case of multipartite numbers is of general application in the subject and is very remarkable. I do not see any other *a priori* proof of it at the moment of writing.

Art. 18. In general, we consider the case in which no constituent of the multipartite parts is to exceed the integer j. We strike out from the functions Q all partitions which involve numbers exceeding j and reach the infinite series of functions

$$\mathbf{J}_1, \ \mathbf{J}_2, \ \dots \ \mathbf{J}_i \ \dots$$

These functions are operated upon in the manner

$$\mathbf{D}_{i}\mathbf{J}_{i} = \mathbf{D}_{2i}\mathbf{J}_{i} = \mathbf{D}_{3i}\mathbf{J}_{i} = \ldots = \mathbf{D}_{ii}\mathbf{J}_{i} = \mathbf{J}_{i};$$

while every other Hammond operator causes  $J_i$  to vanish. By the same reasoning as was used in the special cases we find that

$$\mathbf{D}_{m}\mathbf{J}_{1}^{k_{1}}\mathbf{J}_{2}^{k_{2}}\ldots\mathbf{J}_{i}^{k_{i}}=\mathrm{F}_{j}\left(m\;;\;1^{k_{1}}2^{k_{2}}\ldots\;i^{k_{i}}
ight).\;\mathbf{J}_{1}^{k_{1}}\mathbf{J}_{2}^{k_{2}}\ldots\;\mathbf{J}_{i}^{k_{i}},$$

where

$$F_j(m; 1^{k_1}2^{k_2}...i^{k_i})$$

is equal to the coefficient of  $x^m$  in the expansion of the function

$$(1+x+\ldots+x^{j})^{k_1}(1+x^2+\ldots+x^{2j})^{k_2}\ldots(1+x^i+\ldots+x^{ij})^{k_i}$$
,

which, written in CAYLEY's notation, is

$$\left\{\frac{(j+1)}{(1)}\right\}^{k_1}\left\{\frac{(2j+2)}{(2)}\right\}^{k_2}; \cdots \left\{\frac{(ij+i)}{(i)}\right\}^{k_i}.$$

We have

$$\mathbf{F}_{k}(\mathbf{J}) = \mathbf{\Sigma} \frac{\mathbf{J}_{1}^{k_{1}} \mathbf{J}_{2}^{k_{2}} \dots \mathbf{J}_{i}^{k_{k}}}{1^{k_{1}} 2^{k_{2}} \dots i^{k_{i}} k_{1} 1 k_{2} 1 \dots k_{k} 1};$$

and if, in  $F_k(\mathbf{J})$ , we write

$$\frac{(sj+s)}{(s)}$$
 for  $\mathbf{J}_s$ 

we must reach the expression

$$\frac{(k+1)(k+2)...(k+j)}{(1)(2)...(j)} \text{ otherwise written } \frac{(j+1)(j+2)...(j+k)}{(1)(2)...(k)}.$$

For the rest the enumeration, connected with this restriction, proceeds  $pari\ passu$  with the special cases involving the values of  $j, \infty, 1, 2$ , which have been already examined.

Art. 19. Coming now to the last stage of the investigation we have for consideration the partitions of multipartite numbers in which the constituents of the multipartite parts must be drawn from the particular set of numbers

$$u_1, u_2, \dots u_s$$
.

The partitions involved in the first function U, of the infinite series

$$\mathbf{U}_1, \ \mathbf{U}_2, \ \mathbf{U}_3, \ \dots \ \mathbf{U}_k, \ \dots$$

must involve the numbers  $u_1, u_2, \dots u_s$ , and no others.

Thus

$$\mathbf{U}_{1} = 1 + (u_{1}) + (u_{1}^{2}) + (u_{2}) + (u_{1}^{3}) + (u_{1}u_{2}) + (u_{3}) + \dots \text{ ad inf.},$$

$$\mathbf{U}_{2} = 1 + (2u_{1}) + (2u_{1}2u_{1}) + (2u_{2}) + (2u_{1}2u_{1}) + (2u_{1}2u_{2}) + (2u_{3}) + \dots \text{ ad inf.},$$

$$\mathbf{U}_i = 1 + (iu_1) + (iu_1iu_1) + (iu_2) + (iu_1iu_1iu_1) + (iu_1iu_2) + (iu_3) + \dots$$
 ad inf.

Clearly

$$\mathrm{D}_{\textit{u}_1} \textbf{U}_1 = \mathrm{D}_{\textit{u}_2} \textbf{U}_1 = \ldots = \mathrm{D}_{\textit{u}_s} \textbf{U}_1 = \textbf{U}_1 \,;$$

and any other Hammond operator causes U<sub>1</sub> to vanish.

Also

$$D_{iu_i}\mathbf{U}_i = D_{iu_2}\mathbf{U}_i = \dots = D_{iu_i}\mathbf{U}_i = \mathbf{U}_i;$$

and any other Hammond operator causes  $U_i$  to vanish.

We have presented to us the generating function

$$\begin{aligned} & 1 + a\mathbf{U}_{1} \\ & + \frac{a^{2}}{2!}(\mathbf{U}_{1}^{2} + \mathbf{U}_{2}) \\ & + \frac{a^{3}}{3!}(\mathbf{U}_{1}^{3} + 3\mathbf{U}_{1}\mathbf{U}_{2} + 2\mathbf{U}_{3}) \\ & + \dots \\ & + a^{k}\mathbf{F}^{k}(\mathbf{U}) \\ & + \dots \end{aligned}$$

where

$$\mathbf{F}_{k}(\mathbf{U}) = \mathbf{\Sigma}' \frac{\mathbf{U}_{1}^{k_{1}} \mathbf{U}_{2}^{k_{2}} \dots \mathbf{U}_{i}^{k_{i}}}{1^{k_{1}} \cdot 2^{k_{2}} \dots i^{k_{i}} \cdot k_{1} \mid k_{2} \mid \dots k_{i} \mid} \cdot$$

The effect of  $D_m$  upon the product

$$\mathbf{U}_1^{k_1}\mathbf{U}_2^{k_2}\dots \mathbf{U}_i^{k_i}$$

is to multiply it by the coefficient of  $x^m$  in the function

$$(1+x^{u_1}+x^{u_2}+\ldots+x^{u_s})^{k_1}(1+x^{2u_1}+x^{2u_2}+\ldots+x^{2u_s})^{k_2}\ldots(1+x^{iu_1}+x^{iu_2}+\ldots+x^{iu_s})^{k_i},$$

which I write in the abbreviated notation

$$X_u^{k_1}X_{2u}^{k_2}\dots X_{iu}^{k_i}$$

If in the expression of  $F_k(\mathbf{U})$  we write  $X_{su}$  for  $\mathbf{U}_s$  we must reach the expression which enumerates the partitions of unipartite numbers into k or fewer parts, such parts being drawn from the series  $u_1, u_2, u_3 \dots u_s$ . That is to say we must arrive at the coefficient of  $a^k$  in the expansion of

$$\frac{1}{(1-a)(1-ax^{u_1})(1-ax^{u_2})\dots(1-ax^{u_s})}.$$

Hence this coefficient has the expression

$$\Sigma \frac{X_u^{k_1}X_{2u}^{k_2}...X_{iu}^{k_i}}{1^{k_1}...2^{k_2}...i^{k_i}.k_1!k_2!...k_i!}.$$

To enumerate the partitions we have

$$D_{m_1}F_k(\mathbf{U}) = \sum \frac{F_u(m_1; 1^{k_1}2^{k_2}\dots i^{k_i})}{1^{k_1} \cdot 2^{k_2} \cdot \dots i^{k_i} \cdot k_1! k_2! \cdot \dots k_i!} \mathbf{U}_1^{k_1}\mathbf{U}_2^{k_2} \cdot \dots \mathbf{U}_i^{k_i},$$

where  $F_{\mu}(m_1; 1^{k_1}2^{k_2}...i^{k_i})$  is equal to the coefficient of  $x^{m_1}$  in

and thence the number of partitions of the multipartite number

$$m_1 m_2 \dots m_s$$

into k or fewer parts, such parts being drawn exclusively from the series

 $\sum \frac{\mathrm{F}_{u}\left(m_{1};\ 1^{k_{1}}2^{k_{2}}\ldots i^{k_{i}}\right).\ \mathrm{F}_{u}\left(m_{2};\ 1^{k_{1}}2^{k_{2}}\ldots i^{k_{i}}\right)\ldots\mathrm{F}_{u}\left(m_{s};\ 1^{k_{1}}2^{k_{2}}\ldots i^{k_{i}}\right)}{1^{k_{1}}.\ 2^{k_{2}}\ldots i^{k_{i}}.\ k_{2}\mid k_{2}\mid\ldots k_{r}\mid}$ 

 $u_1, u_2, \dots u_s,$ 

the summation being in regard to the partitions of k.

As an example, I will consider partitions of multipartite numbers where the numbers which are constituents of the multipartite parts are limited to be either 3, 5, or 7. For the partitions into three or fewer parts we have the function

$$\frac{1}{6} (\mathbf{U}_1^3 + 3\mathbf{U}_1\mathbf{U}_2 + 2\mathbf{U}_3),$$

and we have to find the coefficients of  $x^m$  in the three functions

$$(1+x^3+x^5+x^7)^3,$$
  
 $(1+x^3+x^5+x^7)(1+x^6+x^{10}+x^{14}),$   
 $(1+x^9+x^{15}+x^{21}).$ 

Thence, as particular cases,

$$\begin{split} \mathbf{D}_{12}\mathbf{U}_{1}^{3} &= 6\mathbf{U}_{1}^{3}\,; \quad \mathbf{D}_{11}\mathbf{U}_{1}^{3} = 3\mathbf{U}_{1}^{3}\,; \quad \mathbf{D}_{10}\mathbf{U}_{1}^{3} = 9\mathbf{U}_{1}^{3}\,; \\ \mathbf{D}_{12}\mathbf{U}_{1}\mathbf{U}_{2} &= 0\;; \quad \mathbf{D}_{11}\mathbf{U}_{1}\mathbf{U}_{2} = \mathbf{U}_{1}\mathbf{U}_{2}\,; \quad \mathbf{D}_{10}\mathbf{U}_{1}\mathbf{U}_{2} = 0\;; \\ \mathbf{D}_{12}\mathbf{U}_{3} &= \mathbf{D}_{11}\mathbf{U}_{3} = \mathbf{D}_{10}\mathbf{U}_{3} = 0. \\ \mathbf{D}_{12}^{\sigma_{1}}\frac{1}{6}\left(\mathbf{U}_{1}^{3} + 3\mathbf{U}_{1}\mathbf{U}_{2} + 2\mathbf{U}_{3}\right) &= \frac{1}{6}\cdot6^{\sigma_{1}}\mathbf{U}_{1}^{3}, \\ \mathbf{D}_{11}^{\sigma_{2}}\frac{1}{6}\left(\mathbf{U}_{1}^{3} + 3\mathbf{U}_{1}\mathbf{U}_{2} + 2\mathbf{U}_{3}\right) &= \frac{1}{6}\left(6^{\sigma_{2}}\mathbf{U}_{1}^{3} + 3\mathbf{U}_{1}\mathbf{U}_{2}\right), \\ \mathbf{D}_{10}^{\sigma_{3}}\frac{1}{6}\left(\mathbf{U}_{1}^{3} + 3\mathbf{U}_{1}\mathbf{U}_{2} + 2\mathbf{U}_{3}\right) &= \frac{1}{6}\cdot9^{\sigma_{3}}\mathbf{U}_{1}^{3}, \end{split}$$

Thence

is

showing that the multipartite numbers

$$12^{\sigma_1}$$
,  $11^{\sigma_2}$ ,  $10^{\sigma_3}$ ,

have  $6^{\sigma_1-1}$ ,  $\frac{1}{6}(3^{\sigma_2}+3)$ ,  $\frac{1}{6}$ .  $9^{\sigma_3}$  partitions respectively into three or fewer parts.

Also

$$\mathbf{D}_{12}^{\sigma_{1}}\mathbf{D}_{10}^{\sigma_{2}}\mathbf{D}_{10}^{\sigma_{3}}\frac{1}{6}\left(\mathbf{U}_{1}^{3}+3\mathbf{U}_{1}\mathbf{U}_{2}+2\mathbf{U}_{3}\right)=\frac{1}{6}\left(6^{\sigma_{1}}\cdot3^{\sigma_{2}}\cdot9^{\sigma_{3}}\mathbf{U}_{1}^{3}+3\mathbf{U}_{1}\mathbf{U}_{2}\right),$$

where the term  $3\mathbf{U}_1\mathbf{U}_2$  only appears if  $\sigma_1$  and  $\sigma_2$  are both zero.

Hence in general, if  $\sigma_1$  and  $\sigma_2$  are not both zero, the multipartite number

$$12^{\sigma_1}11^{\sigma_2}10^{\sigma_3}$$

possesses  $6^{\sigma_1-1}$ .  $3^{\sigma_2}$ .  $9^{\sigma_3}$  partitions of the nature considered. In particular the multipartite number

12 12 11, for 
$$\sigma_1 = 2$$
,  $\sigma_2 = 1$ ,  $\sigma_3 = 0$ ,

possesses the 18 partitions

(775	553	003),	(755	573	003),	(573	705	053),
(775	053	503),	(575	753	003),	(753	073	505),
(773	555	003),	(755	073	503),	(573	703	055),
(773	553	005),	(575	703	053),	(555	073	703),
(773	505	053),	(753	573	005),	(553	705	073),
(773	055	503),	(753	075	503),	(553	075	703).

Art. 20. In considering the partitions of the multipartite number  $m_1m_2...m_s$  the partitions of the unipartite constituents of the number have been regarded as being subject to the same conditions and restrictions. This, however, is not necessary except in the case of the number of parts which has been denoted by k.

We may for  $m_1$  choose any of the restrictions that have been denoted by the symbols A, B, ... J ... Q, U. For  $m_2$  similarly and so on. For instance, suppose the numbers  $m_1$ ,  $m_2$ ,  $m_3$  are subject to the restrictions denoted by B, Q, and U; that is to say, the partitions of  $m_1$  are such that no part exceeds 2; the partitions of  $m_2$  are unrestricted; the partitions of  $m_3$  are such that the parts are drawn exclusively from specified integers  $u_1$ ,  $u_2$ , ...  $u_s$ .

For the partitions of the multipartite number  $m_1m_2...m_s$ , subject to this combination of restrictions, we

(i.) Take

$$D_{m_1} \sum \frac{\mathbf{B}_{1}^{k_1} \mathbf{B}_{2}^{k_2} \dots \mathbf{B}_{i}^{k_i}}{1^{k_1} 2^{k_2} \dots i^{k_i} \cdot k_1 ! k_2 ! \dots k_i !},$$

with the result

$$\Sigma \operatorname{F}_{b}(m_{1}; 1^{k_{1}}2^{k_{2}}...i^{k_{i}}) \frac{\mathbf{B}_{1}^{k_{1}}\mathbf{B}_{2}^{k_{2}}...\mathbf{B}_{i}^{k_{i}}}{1^{k_{1}}2^{k_{2}}...i^{k_{i}}.k_{1}!k_{2}!...k_{i}!};$$

(ii.) We change the symbol B into the symbol Q and find

$$\begin{split} \mathbf{D}_{m_{2}} \sum \mathbf{F}_{b} \left( m_{1} \; ; \; 1^{k_{1}} 2^{k_{2}} \ldots i^{k_{i}} \right) & \frac{\mathbb{Q}_{1}^{k_{1}} \mathbb{Q}_{2}^{k_{2}} \ldots \mathbb{Q}_{i}^{k_{i}}}{1^{k_{1}} 2^{k_{2}} \ldots i^{k_{i}} \cdot k_{1} \mid k_{2} \mid \ldots k_{i} \mid} \\ &= \sum \mathbf{F}_{b} \left( m_{1} \; ; \; 1^{k_{1}} 2^{k_{2}} \ldots i^{k_{i}} \right) \cdot \mathbf{F}_{q} \left( m_{2} \; ; \; 1^{k_{1}} 2^{k_{2}} \ldots i^{k_{i}} \right) \frac{\mathbb{Q}_{1}^{k_{1}} \mathbb{Q}_{2}^{k_{2}} \ldots \mathbb{Q}_{i}^{k_{i}}}{1^{k_{1}} 2^{k_{2}} \ldots i^{k_{i}} \cdot k_{1} \mid k_{2} \mid \ldots k_{i} \mid}; \end{split}$$

(iii.) Lastly we change the symbol Q into the symbol U and find that

$$\begin{split} &\mathbf{D}_{\textit{m}_{3}} \boldsymbol{\Sigma} \; \mathbf{F}_{\textit{b}} \left(m_{1} \; ; \; 1^{k_{1}} 2^{k_{2}} \ldots i^{k_{i}} \right) . \; \mathbf{F}_{\textit{q}} \left(m_{2} \; ; \; 1^{k_{1}} 2^{k_{2}} \ldots i^{k_{i}} \right) \frac{\mathbf{U}_{1}^{k_{1}} \mathbf{U}_{2}^{k_{2}} \ldots \mathbf{U}_{i}^{k_{i}}}{1^{k_{1}} 2^{k_{2}} \ldots i^{k_{i}} . \; k_{1} ! \; k_{2} ! \ldots k_{i} !} \\ &= \boldsymbol{\Sigma} \; \mathbf{F}_{\textit{b}} \left(m_{1} \; ; \; 1^{k_{1}} 2^{k_{2}} \ldots i^{k_{i}} \right) . \; \mathbf{F}_{\textit{q}} \left(m_{2} \; ; \; 1^{k_{1}} 2^{k_{2}} \ldots i^{k_{i}} \right) . \; \mathbf{F}_{\textit{u}} \left(m_{3} \; ; \; 1^{k_{1}} 2^{k_{2}} \ldots i^{k_{i}} \right) \frac{\mathbf{U}_{1}^{k_{1}} \mathbf{U}_{2}^{k_{2}} \ldots \mathbf{U}_{i}^{k_{i}}}{1^{k_{1}} 2^{k_{2}} \ldots i^{k_{i}} . \; k_{1} ! \; k_{2} ! \ldots k_{i} !}, \end{split}$$

and herein putting  $\mathbf{U}_1 = \mathbf{U}_2 = \dots = \mathbf{U}_i = 1$ , we reach the conclusion that the multipartite number  $m_1 m_2 \dots m_s$  has

$$\sum \frac{F_b(m_1; 1^{k_1}2^{k_2}\dots i^{k_i}) \cdot F_q(m_2; 1^{k_1}2^{k_2}\dots i^{k_i}) \cdot F_u(m_3; 1^{k_1}2^{k_2}\dots i^{k_i})}{1^{k_1}2^{k_2}\dots i^{k_i} \cdot k_1 ! k_2 ! \dots k_i !}$$

partitions of the nature we are considering.





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BY

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# V. On the Kinetic Theory of a Gas. Part II.—A Composite Monatomic Gas: Diffusion, Viscosity, and Thermal Conduction.

By S. Chapman, M.A., D.Sc., Fellow and Lecturer of Trinity College, Cambridge.

### Communicated by Sir Joseph Larmor, F.R.S.

#### Received May 19,—Read June 29, 1916.

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#### Introduction.\*

The present memoir was originally intended to deal only with the theory of diffusion, which still remains its chief subject. During the course of the work, however, it became clear that the theory of viscosity and thermal conduction could also be incorporated by a slight extension of the analysis. This has been done, and the paper now affords an account of all these three "ordinary" mean-free-path phenomena of a composite gas.

The treatment of viscosity and conduction is brief, partly because the theory for a composite gas is so much more complex and less important than that for

a simple gas.\* For the same reason the results are not carried to a higher degree of approximation than that attained, in regard to the same phenomena, in an earlier memoir.† The present method, however, enables the approximation to be carried to any degree of accuracy, which was not formerly possible. Also a certain mistake in the previous investigation of the conductivity of a composite gas is indicated and corrected  $(cf. \S 18)$ .

By its very nature, the problem of diffusion requires the consideration of molecules of two kinds, a complication which is unnecessary in the construction of a theory of viscosity and conduction. Perhaps this circumstance largely explains the greater progress which had hitherto been made in the latter theory, as compared with the theory of diffusion. Until recently the only accurate expression which had been obtained for the coefficient of diffusion D<sub>12</sub> was that deduced by MAXWELL in his second great memoir ton the dynamical theory; it referred exclusively to a gas whose molecules inter-act according to the inverse fifth-power law of force. The best available value of D<sub>12</sub> for molecules of other kinds was due to Langevin, but the formula, unlike MAXWELL'S, was only approximate. It was determined on the assumption that the distribution of velocities in each group of molecules, relative to the mean velocity of the group, was according to Maxwell's well-known law appropriate to a gas in the uniform steady state. The amount of error (if any) introduced by this assumption was unknown. In the present paper the true law of distribution is determined, and an exact expression is obtained for D<sub>12</sub> which is applicable to the most general case of a composite monatomic gas. It is found on comparison that the error of the above approximate formula is as great as 13 per cent. in extreme cases ( $\S 13 (e)$ ).

A particular case of Langevin's formula, relating to rigid elastic spherical molecules, had previously been deduced by Stefan in 1871. The theories of Maxwell, Stefan, Boltzmann,\*\* and Langevin, and my own earlier theory, all agreed in predicting no change in  $D_{12}$  with the relative proportion of the two sets of molecules. Another theory, originated by Meyer††, asserted that there would be a large variation in  $D_{12}$  as the proportion of either component varied from 0 to 1.

- \* This has been dealt with in detail in my recent memoir, 'Phil. Trans.,' A, vol. 216, pp. 279-348, 1915.
- † 'Phil. Trans.,' A, vol. 211, pp. 433–483, 1911.
- ‡ MAXWELL, 'Collected Works,' ii., p. 27. His formula for  $D_{12}$  is a special case of the general result (13.03) of this paper.
- § Langevin, 'Ann. de Chimie et de Physique,' (8), v., 245 (1905); cf. also Enskog, 'Phys. Zeit.,' xii., 533 (1911). The same result was independently discovered by the present writer, 'Phil. Trans.,' A vol. 211, p. 499 (1911).
  - || Maxwell, 'Collected Works,' i., p. 392; ii., p. 57, p. 345.
  - ¶ Stefan, 'Wien. Sitzb.,' 63, (2), p. 63, 1871; 65, p. 323, 1872.
- \*\* Boltzmann, 'Wien. Sitzb.,' 66, p. 324, 1872; 78, p. 733, 1878; 86, p. 63, 1882; 88, p. 835, 1883; also 'Vorlesungen,' i., p. 96.
- †† MEYER, 'Kinetic Theory of Gases,' p. 255 (English ed.); also Gross, 'Wied. Ann.,' 40, p. 424, 1890.

The experimental data which were determined in order to test the point confirmed neither conclusion; a variation in  $D_{12}$  was observed, but it was so much smaller than that suggested by Meyer's formula that the experimental values of  $D_{12}$  were in closer numerical agreement with a constant expression than with Meyer's highly variable result. Recently Kuenen\* has modified Meyer's theory by taking into account the tendency of a molecule to persist in its original direction after collision, a consideration the importance of which was brought into prominence by Jeans† in connection with the elastic-sphere theory of viscosity. As a result of this revision Meyer's theory is brought much more closely into accord with experiment (§ 13 (i)), though the discrepancies still exceed those between the observed values of  $D_{12}$  and a suitable constant mean.

In § 13 (i) the observations of D<sub>12</sub> relating to the above variations are compared also with the results of the present theory, which affords a formula similar to that of Langevin but multiplied by a correction factor which is a function of the relative proportions of the component gases. The agreement with experiment, while not exact, is perhaps as close as the degree of experimental errors, and the uncertainty as to the best molecular model, entitle us to expect.

The present theory of diffusion is compared also, in two particular cases, with exact results obtained theoretically by other writers. These cases are (a) that of a gas formed of two sets of molecules which are identical in their dynamical properties (as in the problem of the self diffusion of a gas), and (b) that of a gas in which the molecules of one kind are infinitesimal in size and mass compared with those of the other kind (as in electronic diffusion in gases). These problems have been dealt with respectively by PIDDUCK‡ and LORENTZ§; the corresponding special forms of the general expressions here deduced are in satisfactory accordance with their results (§ 13 (e), (f)).

Certain other phenomena connected with diffusion are also discussed which do not seem to have been investigated in any detail hitherto. In §§ 10, 14, 15 it is shown that diffusion may be produced by a gradient of pressure or temperature independently of the presence of a concentration gradient or of external forces; in §§ 14, 15 the amount of this effect is considered, with numerical illustrations relating to particular pairs of gases. Conversely, the absence of diffusion in a composite gas in which the temperature is non-uniform (the pressure being uniform and there being no external forces) implies the existence of a corresponding variation in the relative concentration of the two gases. This latter variation  $(cf. \S 16)$  appears to be so large in amount

<sup>\*</sup> KUENEN, 'Supp. No. 8 to the Communications from the Leyden Physical Laboratory,' January, 1913; also 'Amsterdam Acad. Proc.,' 16, p. 1162, 1914.

<sup>†</sup> Jeans, 'Dynamical Theory of Gases' (2nd ed.), pp. 276, 292, 328.

<sup>†</sup> PIDDUCK, 'Proc. Lond. Math. Soc.' (2), 15, p. 89, 1915.

<sup>§</sup> LORENTZ, 'Archives Nécrlandaises,' 10, p. 336, 1905; 'Theory of Electrons,' p. 268. More general results obtained by Jeans, using Lorentz's method, are given in his 'Dynamical Theory of Gases,' 2nd ed., §§ 314, et seq. Cf. also Pidduck, loc. cit., p. 112.

as to suggest a doubt whether some compensating influence has not been overlooked in the theory, and it is desirable that the matter should be put to the test of experiment (see Note A, p. 196). In §§ 12, 19, it is shown that diffusion is necessarily accompanied by a transfer of thermal energy, and a new physical constant, the "specific energy of diffusion," is introduced and discussed.

The method used to determine the velocity-distribution function is similar to that published in my recent memoir on a simple gas; the details of the work are, of course, more complicated in the present case. The formulation of the equations of diffusion and energy for a composite gas, executed in §§ 10 and 12, embodies certain features which seem to be novel.

We may here remark also upon some by-products of the analysis which suggest interesting developments in the field of pure mathematics. The comparison of Lorentz's solution of the problem of electronic diffusion with my own has led to expressions for  $\pi$  and  $\sin \pi x$  of an altogether new form. Lorentz used Boltzmann's integral equation for the velocity-distribution function, and obtained a solution in finite terms involving  $\pi$ ; the solution arrived at in this paper is determined by the use of the aggregate of the equations of transfer (§ 2), which is really equivalent to Boltzmann's equation. The result is expressed, however, in terms of the quotient of a symmetrical infinite determinant by its principal minor, and formulæ of this kind are hence found for  $\pi$  (and also for  $\sin \pi x$ ). The elements of the determinant are expressible simply, in terms of gamma functions. A further study of the subject from the analytical point of view would probably be fruitful in results of interest and importance (see Note B, p. 196).

I hope later to apply the present methods to the examination of the problems offered by rarefied gases. So far, however, as concerns the mean-free-path phenomena in monatomic gases under *normal* conditions, the investigation imperfectly attempted in my memoir of 1911 is completed by this and the second paper already referred to ('Phil. Trans.,' A, vol. 216).

It is a pleasure here to make grateful acknowledgment of my indebtedness to Sir Joseph Larmor throughout these investigations, which were started under his influence, and would hardly have been carried to this stage but for the inspiration afforded by his continued encouragement and interest.

# § 1. Analysis of the Dynamical State of a Composite Gas.

# (a) Notation.\*\*

The gas considered in this paper is one composed of molecules of two kinds, each having the property of spherical symmetry (or, in brief, each being "monatomic").

\* In numbering the equations I have adopted the decimal method introduced by Peano. The number to the left of the decimal point is the number of the section, and within any section the numbers to the right, if read as decimals, are in numerical order. With this method it is possible, by the introduction of a third or even fourth figure, to number equations inserted between others already numbered, without having to alter the references to all succeeding equations.

The density of the gas is supposed to be such that the mean free path of a molecule is large compared with the distance at which molecules appreciably affect one another's trajectories: this we express concisely by terming the gas "nearly perfect."

Similar quantities relating to the two groups of molecules will be represented by similar symbols, with distinguishing suffixes 1, 2; it is convenient to adopt the convention that the first gas is that which has the greater molecular mass. The molecular masses will be denoted by  $m_1$ ,  $m_2$ , while the notation for various other characteristics of the gas at  $(x, y, z, t)^*$  is explained by the following list:

 $\nu_1$ ,  $\nu_2 \equiv$  the number of molecules of the first and second kinds per unit volume.

 $\lambda_1, \lambda_2 \equiv$  the proportion of molecules of each kind at (x, y, z, t).

 $\rho_1, \rho_2 \equiv$  the densities of the constituent gases.

 $P_1$ ,  $P_2 \equiv$  the external forces (in vector notation) acting on each molecule  $m_1$ ,  $m_2$ .

 $(X_1, Y_1, Z_1), (X_2, Y_2, Z_2) \equiv$  the same forces in Cartesian notation.

 $c_1$ ,  $c_2$  or  $(u_1, v_1, w_1)$ ,  $(u_2, v_2, w_2) \equiv$  the mean velocities of the two groups of molecules in vector or Cartesian notation.

We define further quantities of the same nature, in terms of the above, as follows:—

(1.01) 
$$\nu_0 \equiv \nu_1 + \nu_2$$
, so that  $\lambda_1 = \nu_1/(\nu_1 + \nu_2) = \nu_1/\nu_0$ ,  $\lambda_2 = \nu_2/(\nu_1 + \nu_2) = \nu_2/\nu_0$ ,  $\lambda_1 + \lambda_2 = 1$ .

(1.02) 
$$2\lambda'_0 \equiv \lambda_1 - \lambda_2$$
,  $\lambda_{12} \equiv \lambda_1/\lambda_2$ ,  $\lambda_{21} \equiv \lambda_2/\lambda_1$ , so that  $\lambda_{12}\lambda_{21} = 1$ .

(1.03) 
$$m_0 \equiv \lambda_1 m_1 + \lambda_2 m_2$$
,  $m'_0 \equiv \lambda_1 (m_1 - m_0) = -\lambda_2 (m_2 - m_0) = \lambda_1 \lambda_2 (m_1 - m_2)$ .

Now we have

$$\rho_1 = \nu_1 m_1, \qquad \rho_2 = \nu_2 m_2,$$

so that, by (1.01) and (1.03),

(1.05) 
$$\rho_0 \equiv \rho_1 + \rho_2 = \nu_1 m_1 + \nu_2 m_2 = \nu_0 m_0, \qquad \rho'_0 \equiv \frac{\nu_0 m'_0}{\lambda_1 \lambda_2} = \nu_0 (m_1 - m_2).$$

Also, in vector notation P, c, we shall write

(1.06) 
$$P_0 \equiv \lambda_1 P_1 + \lambda_2 P_2$$
,  $P'_0 \equiv \lambda_1 \left( P_1 - \frac{m_1}{m_0} P_0 \right) = -\lambda_2 \left( P_2 - \frac{m_2}{m_0} P_0 \right) = \lambda_1 \lambda_2 \left( \frac{m_2}{m_0} P_1 - \frac{m_1}{m_0} P_2 \right)$ .

(1.07) 
$$c_0 \equiv \lambda_1 c_1 + \lambda_2 c_2$$
,  $c'_0 \equiv \lambda_1 (c_1 - c_0) = -\lambda_2 (c_2 - c_0) = \lambda_1 \lambda_2 (c_1 - c_2)$ .

<sup>\*</sup> I.e., at the point (x, y, z) and at time t.

The corresponding component equations, involving X, Y, Z or u, v, w with appropriate suffixes, are similar and will not be written down here.

By inverting the above equations we obtain the following expressions for the original in terms of the derived quantities:—

(1.08) 
$$m_1 = m_0 + \frac{m'_0}{\lambda_1}, \qquad P_1 = \frac{m_1}{m_0} P_0 + \frac{P'_0}{\lambda_1}, \qquad c_1 = c_0 + \frac{c'_0}{\lambda_1}.$$

(1.09) 
$$m_2 = m_0 - \frac{m'_0}{\lambda_2}, \quad P_2 = \frac{m_2}{m_0} P_0 - \frac{P'_0}{\lambda_2}, \quad c_2 = c_0 - \frac{c'_0}{\lambda_2}.$$

# (b) The Interpretation of the Derived Quantities.

Corresponding to (1.08) and (1.09), the motion of the gas can be analysed into (a) a steady motion of the composite gas as a whole with velocity  $c_0$ , together with (b) a motion of interdiffusion in which the mean velocities of the two streams are respectively  $c'_0/\lambda_1$  and  $-c'_0/\lambda_2$ . In this latter motion equal numbers of molecules are transferred per unit time in each direction, the number (per unit area normal to the direction of the vector  $c'_0$ ) being  $\nu_0 c'_0$ , since by (1.01)

$$(1.10) v_1 c'_0 / \lambda_1 = v_2 c'_0 / \lambda_2 = v_0 c'_0.$$

The momentum of the common motion (a) is clearly  $\rho_0 c_0$  per unit volume, while that of the motion of interdiffusion is  $\nu_0 (m_1 - m_2) c'_0$  or, by (1.05),  $\rho'_0 c'_0$ ; in general this is not zero, owing to the inequality of mass of the molecules, although the diffusing streams convey equal numbers of them in any interval of time. This analysis of momentum corresponds to the equation

$$(1.11) \rho_1 c_1 + \rho_2 c_2 = \nu_1 m_1 c_1 + \nu_2 m_2 c_2 = \rho_0 c_0 + \rho'_0 c'_0.$$

The equations (1.06) differ from the others by involving the molecular masses as well as  $v_1$  and  $v_2$ . This resolution of the forces  $P_1$  and  $P_2$  may be considered as follows: the first terms (cf. 1.08 and 1.09), viz.,  $\frac{m_1}{m_0}P_0$  on  $m_1$  and  $\frac{m_2}{m_0}P_0$  on  $m_2$ , represent forces which will impart a common acceleration  $P_0/m_0$  to each group of molecules (we may regard this variation as affecting their common velocity of streaming,  $c_0$ ); the remaining components,  $P'_0/\lambda_1$  on  $m_1$  and  $-P'_0/\lambda_2$  on  $m_2$ , when summed up over the  $v_1$ ,  $v_2$  molecules of the corresponding groups, afford equal and opposite total forces  $v_0P'_0$ ,  $v_0P'_0$ . In connection with this we may remember that two such interdiffusing groups of molecules as we have considered will exert equal and opposite actions on one another, and that equal and opposite forces must be applied to the two groups if their motion of interdiffusion is to be maintained, or modified without imparting any common velocity to them.

As regards  $\lambda'_0$ , this is useful for the purpose of imparting a symmetrical form to some of our equations; if D denotes a differential operator of any kind with respect to (x, y, z, t), since  $\lambda_1 + \lambda_2 = 1$  we have, by (1.02),

(c) The "Peculiar" Motions of the Molecules.

So far we have been concerned with the *mean* velocities of the constituents of the gas, without considering the actual motions of individual molecules. We shall denote the velocities of typical molecules of the two kinds by  $(c)_1$ ,  $(c)_2$  or  $\{(u)_1, (v)_1, (w)_1\}$ ,  $\{(u)_2, (v)_2, (w)_2\}$ , when referred to the co-ordinate axes, or, when referred to axes moving with the velocity  $c_0$  appropriate to the point and time in question, by  $C_1$ ,  $C_2$  or  $(U_1, V_1, W_1)$ ,  $(U_2, V_2, W_2)$ . Thus

(1.13) 
$$C_1 = (c)_1 - c_0, \qquad C_2 = (c)_2 - c_0.$$

The velocities C<sub>1</sub>, C<sub>2</sub> will be called the "peculiar" velocities of the molecules.

We have no means of determining the individual values of  $C_1$ ,  $C_2$  for the molecules near (x, y, z, t), but for a given state of the gas, as specified by its composition, mean motions, pressures, and temperature (these are expressible in terms of mean values of functions of C), there will be a certain frequency law, or function representing the distribution of various values of the velocity among the molecules. The determination of this velocity-distribution function is fundamental in the method of this paper. It will clearly involve C or its components as independent variables, together with certain parameters (e.g., pressures or mean velocities) which are dependent on (x, y, z, t).

The mean value of any function of the molecular velocities will be denoted by placing a bar over the expression representing the function. Thus, for instance (cf. 1.07),

$$(1.14) \quad (\overline{c})_1 = c_1, \ \overline{(c)}_2 = c_2, \ \overline{C}_1 = \overline{(c)}_1 - c_0 = c_1 - c_0 = c_0 / \lambda_1, \ \overline{C}_2 = \overline{(c)}_2 - c_0 = c_2 - c_0 = -c_0 / \lambda_2.$$

It is convenient at this stage to modify the meaning of our symbols C<sub>1</sub>, C<sub>2</sub>, which have so far represented vector quantities; henceforward they will denote not the vectors themselves, but their amplitudes. These, of course, are essentially positive, scalar quantities. Thus

(1.15) 
$$C_1^2 = U_1^2 + V_1^2 + W_1^2, \qquad C_2^2 = U_2^2 + V_2^2 + W_2^2.$$

The mean energy of peculiar motion per molecule is  $\frac{1}{2}m\overline{C^2}$ , and we shall write

(1.16) 
$$m_{1}\overline{\mathrm{C}_{1}}^{2} \equiv \frac{3}{2h_{1}} \equiv 3\mathrm{RT}_{1}, \qquad m_{2}\overline{\mathrm{C}_{2}}^{2} \equiv \frac{3}{2h_{2}} \equiv 3\mathrm{RT}_{2},$$

where R is the "universal gas constant." These equations define h and T; we shall call  $T_1$ ,  $T_2$  the absolute temperatures of the component gases. According to the theorem of equipartition of energy, in the uniform steady state of a gas they are equal. In the slightly disturbed states which we shall consider, the differences  $h_1-h_2$ ,  $T_1-T_2$  will be small.\*

We further define  $p_1$ ,  $p_2$ ,  $p_0$ , the mean hydrostatic pressures of the separate components of the gas, and of the total gas, by the equations

(1.17) 
$$p_1 \equiv \frac{1}{3}\nu_1 m_1 \overline{C_1}^2 = \frac{\nu_1}{2h_1} = R\nu_1 T_1, \qquad p_2 \equiv \frac{1}{3}\nu_2 m_2 \overline{C_2}^2 = \frac{\nu_2}{2h_2} = R\nu_2 T_2,$$

(1.18) 
$$p_0 \equiv p_1 + p_2 = \frac{\nu_1}{2h_1} + \frac{\nu_2}{2h_2} \equiv \frac{\nu_0}{2h_0} \equiv R\nu_0 T_0.$$

The last equation also defines  $h_0$  and  $T_0$ ; the latter will be called the absolute temperature of the composite gas. Clearly

(1.181) 
$$T_0 = \lambda_1 T_1 + \lambda_2 T_2, \qquad \frac{1}{h_0} = \frac{\lambda_1}{h_1} + \frac{\lambda_2}{h_2}.$$

We shall define  $T'_0$ ,  $p'_0$ ,  $h'_0$  by the equations

$$(1.182) T_0' = \lambda_1 (T_1 - T_0) = -\lambda_2 (T_2 - T_0) = \lambda_1 \lambda_2 (T_1 - T_2),$$

$$\frac{1}{h'_0} = \lambda_1 \left( \frac{1}{h_1} - \frac{1}{h_0} \right) = -\lambda_2 \left( \frac{1}{h_2} - \frac{1}{h_0} \right) = \lambda_1 \lambda_2 \left( \frac{1}{h_1} - \frac{1}{h_2} \right),$$

(1.184) 
$$p'_{0} = \frac{\nu_{0}}{2h'_{0}} = \lambda_{1}\lambda_{2}\left(\frac{p_{1}}{\lambda_{1}} - \frac{p_{2}}{\lambda_{2}}\right) = R\nu_{0}T'_{0}.$$

The following equations are inverse to the above:—

(1.185) 
$$T_1 = T_0 + \frac{T'_0}{\lambda_1}, \qquad T_2 = T_0 - \frac{T'_0}{\lambda_2},$$

(1.186) 
$$p_1 = \lambda_2 (p_0 + \lambda_1 p'_0), \qquad p_2 = \lambda_1 (p_0 - \lambda_2 p'_0).$$

\* [In the paper as originally communicated, no account was taken of these differences, a preliminary examination having indicated that they do not materially affect the theory of diffusion. The distinction between  $T_1$  and  $T_2$  has been re-introduced at the suggestion of a referee, in order that its influence, if any, on the phenomenon of thermal diffusion might be made clear. It will appear that  $T_1 - T_2$  is a small multiple of the rate of change of  $\lambda'_0$  (or  $\lambda_1$ ) with time, so that in steady states of the gas it is a small quantity of the second order only; in particular, the phenomenon dealt with in §16 is unaffected.

Throughout the paper, wherever a distinction is made between  $h_1$  and  $h_2$ ,  $T_1$  and  $T_2$ , or wherever  $T'_0$  (equation 1·182) appears, this has been introduced on revision (June, 1916). The original form of the equations may be found by making the difference zero. An appendix has also been added on account of this extension.—June 2, 1916.]

# (d) Some Convenient Limitations of the Problem.

Our immediate aim is to determine functions  $f_1(U_1, V_1, W_1)$ ,  $f_2(U_2, V_2, W_2)$  which define the distribution of the peculiar velocities of the molecules, *i.e.*, which are such that the number of molecules of the group considered (the appropriate suffix 1 or 2 being added throughout), the components of whose velocities lie between (U, V, W) and (U+dU, V+dV, W+dW) respectively, is

per unit volume. Besides the independent variables U, V, W, these functions f(U, V, W) will also involve such quantities as  $\nu$ ,  $\lambda$ , P, c, h and their derivatives, all of which are functions of (x, y, z, t). The distribution of the peculiar velocities is, however, clearly unaffected by the absolute magnitude of the mean velocity  $c_0$  (though the same is not true of the derivatives of  $c_0$ ). We may, therefore, legitimately make the simplifying convention that  $c_0 = 0$  at the particular point and time under consideration. This merely amounts to a particular choice of uniformly moving axes of reference, a choice which the laws of dynamics leave quite unrestricted.

Our concern being with problems of molecular rather than mass motion, we shall suppose that the acceleration of the gas as a whole is of the first order only, which requires that the resultant force on unit mass of the gas, viz.,  $P_0/m_0$ , shall be small. We shall also suppose throughout that the velocity  $c'_0$  of interdiffusion, and the derivatives, with respect to space and time, of  $\nu$ ,  $\lambda$ , c, h, are all of the first order, at most\*; consequently, since in this paper we shall neglect second order quantities, products and derivatives of any of the small quantities just mentioned will be omitted from our analysis.

### § 2. The Equation of Transfer of Molecular Properties.

# (a) The Equation of Continuity.

The general equation of transfer for a function  $Q_1$  of the velocity components  $(u)_1, (v)_1, (w)_1$  of a molecule of the first kind is†

(2.01) 
$$\Delta Q_{1} = \frac{\partial}{\partial t} \left( \nu_{1} \overline{Q_{1}} \right) + \sum_{x,y,z} \left[ \frac{\partial}{\partial x} \left\{ \nu_{1} \overline{(u)_{1}} \overline{Q_{1}} \right\} - \frac{\nu_{1}}{m_{1}} X_{1} \left\{ \overline{\frac{\partial Q_{1}}{\partial (u)_{1}}} \right\} \right],$$

where  $\Delta Q_1$  denotes the rate of change of  $\nu_1 \overline{Q_1}$  at (x, y, z, t) produced by the encounter of the molecules of the first kind with others of the same or the other kind.

- \* [And likewise  $p'_0$ ,  $T'_0$ ,  $1/h'_0$ , when we are considering unsteady states in which  $T_1 \neq T_2$ .—June 2, 1916.]
- † Cf. Chapter IX. of JEANS' 'Treatise' (2nd ed.), and also, for the details of the reduction of (2.01)-(2.02) and (2.09), 'Phil. Trans.,' A, vol. 216, p. 285.

If we write Q = 1, since  $\Delta Q_1 = 0$ , and  $\frac{\partial Q_1}{\partial (u)_1} = 0$ , the equation of transfer reduces to

(2.011) 
$$\frac{\partial \nu_1}{\partial t} + \frac{\partial (\nu_1 u_1)}{\partial x} + \frac{\partial (\nu_1 v_1)}{\partial y} + \frac{\partial (\nu_1 w_1)}{\partial z} = 0,$$

which is the equation of continuity for the first component of the composite gas. By adding to this the corresponding equation for the second component, we obtain the equation of continuity for the gas as a whole, in the form

or
$$\frac{\partial (\nu_1 + \nu_2)}{\partial t} + \frac{\partial (\nu_1 u_1 + \nu_2 u_2)}{\partial x} + \frac{\partial (\nu_1 v_1 + \nu_2 v_2)}{\partial y} + \frac{\partial (\nu_1 w_1 + \nu_2 w_2)}{\partial z} = 0$$

$$\frac{\partial \nu_0}{\partial t} + \frac{\partial (\nu_0 u_0)}{\partial x} + \frac{\partial (\nu_0 v_0)}{\partial y} + \frac{\partial (\nu_0 w_0)}{\partial z} = 0.$$

If at the point under consideration the mean velocity of the gas is zero, the last equation may be written

(2.013) 
$$\frac{1}{\nu_0} \frac{\partial \nu_0}{\partial t} = -\left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}\right).$$

(b) 
$$Q_1 = U_1 C_1^{2s}$$
.

If in the equation of transfer (2.01) we assign to  $Q_1$  the value  $(u)_1(c)_1^{2s}$ , and omit all terms which in a gas of ordinary density are of the second order, we find that

$$(2.02) \ \Delta \cup_{1} C_{1}^{2s} = \frac{1.3.5...(2s+3)}{3} \frac{\nu_{1}}{(2h_{1}m_{1})^{s}} \left[ \frac{\partial u_{0}}{\partial t} + \frac{1}{2h_{1}m_{1}} \frac{1}{\nu_{1}} \frac{\partial \nu_{1}}{\partial x} - \frac{1}{m_{1}} X_{1} + (s+1) \frac{\partial}{\partial x} \left( \frac{1}{2h_{1}m_{1}} \right) \right].$$

We have here used the convention that  $c_0 = 0$  at this particular point and time, so that  $(c)_1$  and  $C_1$  are identical, and, except in differential coefficients,  $c_0$  can be neglected.

If we multiply both sides of (2.02) by  $m_1$ , and add the corresponding equation for the second group of molecules, in the case when s = 0 we obtain the result

$$(2.03) \qquad \Delta \left( m_1 \mathsf{U}_1 + m_2 \mathsf{U}_2 \right) = \left( \nu_1 m_1 + \nu_2 m_2 \right) \frac{\partial u_0}{\partial t} + \left( \frac{1}{2h_1} \frac{\partial \nu_1}{\partial x} + \frac{1}{2h_2} \frac{\partial \nu_2}{\partial x} \right)$$

$$- \left( \nu_1 \mathsf{X}_1 + \nu_2 \mathsf{X}_2 \right) + \left\{ \nu_1 \frac{\partial}{\partial x} \left( \frac{1}{2h_1} \right) + \nu_2 \frac{\partial}{\partial x} \left( \frac{1}{2h_2} \right) \right\}$$

$$= \nu_0 m_0 \frac{\partial u_0}{\partial t} - \nu_0 \mathsf{X}_0 + \frac{\partial}{\partial x} \left( \frac{\nu_1}{2h_1} + \frac{\nu_2}{2h_2} \right)$$

$$= \nu_0 m_0 \frac{\partial u_0}{\partial t} - \nu_0 \mathsf{X}_0 + \frac{\partial p_0}{\partial x},$$

by (1.18). In this equation the left-hand side is the rate of change of the momentum per unit volume of the whole gas at (x, y, z, t) which is produced by encounters between the molecules. Since, however, an encounter between two molecules leaves their combined momentum unchanged,  $\Delta (m_1 \cup_1 + m_2 \cup_2)$  is zero, and consequently

$$\frac{\partial u_0}{\partial t} = \frac{1}{m_0} X_0 - \frac{1}{\nu_0 m_0} \frac{\partial p_0}{\partial x}.$$

This and the two similar equations in y and z are the equations of mean motion of the gas.

We will now apply (2.04) to the elimination of  $\frac{\partial u_0}{\partial t}$  from (2.02). At the same time we shall neglect the difference between  $h_1$  and  $h_0$ ,  $T_1$  and  $T_0$  in products or derivatives, since our equations are to be carried only to the first order of accuracy. Then (2.02) becomes

$$(2.05) \quad \frac{3(2h_0m_1)^s}{1.3.5...(2s+3)} \frac{m_1}{\nu_1} \Delta U_1 C_1^{2s} = \frac{1}{2h_0} \frac{1}{\nu_1} \frac{\partial \nu_1}{\partial x} + \frac{m_1}{m_0} X_0 - X_1 - \frac{m_1}{\nu_0m_0} \frac{\partial p_0}{\partial x} + (s+1) \frac{\partial}{\partial x} \left(\frac{1}{2h_0}\right)$$

$$= \frac{1}{2h_0} \left(\frac{1}{\nu_1} \frac{\partial \lambda_1}{\partial x} + \frac{1}{\nu_0} \frac{\partial \nu_0}{\partial x}\right) + \frac{\partial}{\partial x} \left(\frac{1}{2h_0}\right) - \frac{1}{\lambda_1} X'_0 - \frac{m_1}{\nu_0m_0} \frac{\partial p_0}{\partial x} + s \frac{\partial}{\partial x} \left(\frac{1}{2h_0}\right)$$

$$= \frac{1}{\lambda_1} \left[\frac{1}{2h_0} \frac{\partial \lambda'_0}{\partial x} - X'_0 - \frac{m'_0}{\nu_0m_0} \frac{\partial p_0}{\partial x}\right] + Rs \frac{\partial T_0}{\partial x}.$$

Thus, if we write

(2.06) 
$$\xi'_{0} \equiv \frac{1}{2h_{0}} \frac{\partial \lambda'_{0}}{\partial x} - X'_{0} - \frac{m'_{0}}{\nu_{0} m_{0}} \frac{\partial p_{0}}{\partial x},$$

the equation (2.05) and the corresponding equation for the second set of molecules become

(2.07) 
$$\frac{3(2h_0m_1)^s}{1 \cdot 3 \cdot 5 \dots (2s+3)} m_1 \Delta U_1 C_1^{2s} = \nu_0 \xi'_0 + Rs\nu_1 \frac{\partial T_0}{\partial x},$$

(2.08) 
$$\frac{3(2h_0m_2)^s}{1 \cdot 3 \cdot 5 \dots (2s+3)} m_2 \Delta \cup_2 C_2^{2s} = -\nu_0 \xi'_0 + Rs\nu_2 \frac{\partial T_0}{\partial x}.$$

To this order of approximation, therefore, these equations do not involve T'<sub>0</sub>.

(c) 
$$Q_1 = U_1^2 C_1^{2s}$$
.

When  $Q_1 = \bigcup_1^2 C_1^{2s}$ , the equation of transfer takes the form  $(cf. \S 3 (C))$  of my second paper, loc. cit.)

$$(2.09) \frac{15 (2h_1 m_1)^{s+1}}{1 \cdot 3 \cdot 5 \dots (2s+3)} \Delta U_1^{2} C_1^{2s} = 5\nu_1 \left\{ \frac{1}{\nu_1} \frac{\partial \nu_1}{\partial t} + (s+1) 2h_1 \frac{\partial}{\partial t} \left( \frac{1}{2h_1} \right) \right\} + (2s+5)\nu_1 \left( 3 \frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} \right).$$

Now

$$(2.10) 3 \frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} = \frac{5}{3} \left( \frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} \right) + \frac{2}{3} \left( 2 \frac{\partial u_0}{\partial x} - \frac{\partial v_0}{\partial y} - \frac{\partial w_0}{\partial z} \right)$$
$$= -\frac{5}{3} \frac{1}{v_0} \frac{\partial v_0}{\partial t} + \frac{2}{3} c_{xx}$$

by (2.013), where also we have used the notation indicated by

$$\begin{cases}
c_{xx} = 2 \frac{\partial u_0}{\partial x} - \frac{\partial v_0}{\partial y} - \frac{\partial w_0}{\partial z}, \\
c_{yy} = 2 \frac{\partial v_0}{\partial y} - \frac{\partial v_0}{\partial z} - \frac{\partial u_0}{\partial x}, \\
c_{zz} = 2 \frac{\partial v_0}{\partial z} - \frac{\partial u_0}{\partial x} - \frac{\partial v_0}{\partial y}.
\end{cases}$$

Evidently we have

$$(2.12) c_{xx} + c_{yy} + c_{zz} = 0.$$

By substitution from (2.10) into (2.09), we find that

$$(2.13) \qquad \frac{15(2h_0m_1)^{s+1}}{1\cdot 3\cdot 5\dots (2s+3)} \,\Delta \,\mathsf{U}_1^{\,2}\mathrm{C}_1^{\,2s} = 5\nu_1 \left\{ \frac{1}{\nu_1} \,\frac{\partial \nu_1}{\partial t} + (s+1) \,2h_1 \,\frac{\partial}{\partial t} \left(\frac{1}{2h_1}\right) - \frac{1}{3}(2s+5) \,\frac{1}{\nu_0} \,\frac{\partial \nu_0}{\partial t} \right\} \\ + \frac{2}{3}(2s+5) \,\nu_1 c_{xx}.$$

If we divide both sides of this equation by  $10 \cdot 2h_1$ , and assign the zero value to s, it becomes

$$(2.14) \Delta_{\frac{1}{2}}^{\frac{1}{2}} m_1 U_1^2 = \frac{1}{2} \left\{ \frac{1}{2h_1} \frac{\partial \nu_1}{\partial t} + \nu_1 \frac{\partial}{\partial t} \left( \frac{1}{2h_1} \right) - \frac{5}{3} \frac{\nu_1}{2h_1} \frac{1}{\nu_0} \frac{\partial \nu_0}{\partial t} + \frac{\nu_1}{3h_1} c_{xx} \right\}.$$

On adding to this the corresponding y and z equations, the result is

(2.15) 
$$\Delta_{\frac{1}{2}}^{1}m_{1}C_{1}^{2} = \frac{3}{2}p_{1}\left(\frac{1}{p_{1}}\frac{\partial p_{1}}{\partial t} - \frac{5}{3}\frac{1}{\nu_{0}}\frac{\partial \nu_{0}}{\partial t}\right).$$

There is a similar equation for the second set of molecules, and by addition of the two we get

(2.16) 
$$\Delta \left( \frac{1}{2} m_1 C_1^2 + \frac{1}{2} m_2 C_2^2 \right) = 0 = \frac{3}{2} p_0 \left( \frac{1}{p_0} \frac{\partial p_0}{\partial t} - \frac{5}{3} \frac{1}{\nu_0} \frac{\partial \nu_0}{\partial t} \right),$$

the left-hand side being zero, since energy is conserved throughout molecular

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encounters. The integration of the last equation gives us the equation of state of the gas, viz.,

$$(2.17) p_0 \nu_0^{-5/8} = \text{constant},$$

or

(2.18) 
$$T_{0\nu_0}^{-2/3} = \text{constant}.$$

We will now return to the general case of (2.13); on neglecting the difference between  $h_1$  and  $h_0$ ,  $H_1$  and  $H_0$ , in derivatives and products, the equation becomes

$$(2.19) \qquad \frac{3(2h_{0}m_{1})^{s+1}}{1 \cdot 3 \cdot 5 \dots (2s+3)} \Delta \cup_{1}^{2} C_{1}^{2s} = \nu_{1} \left[ \frac{1}{\nu_{1}} \frac{\partial \nu_{1}}{\partial t} - \frac{1}{\nu_{0}} \frac{\partial \nu_{0}}{\partial t} + (s+1) \left\{ 2h_{0} \frac{\partial}{\partial t} \left( \frac{1}{2h_{0}} \right) - \frac{2}{3} \frac{1}{\nu_{0}} \frac{\partial \nu_{0}}{\partial t} \right\} \right] + \frac{2}{15} (2s+5) \nu_{1} c_{xx}$$

$$= \nu_{0} \frac{\partial \lambda'_{0}}{\partial t} + \frac{2}{15} (2s+5) \nu_{1} c_{xx}$$

by (2.18). The similar equation for the second set of molecules is

(2.20) 
$$\frac{3(2h_0m_2)^{s+1}}{1 \cdot 3 \cdot 5 \dots (2s+3)} \Delta U_2^2 C_2^{2s} = -\nu_0 \frac{\partial \lambda'_0}{\partial t} + \frac{2}{1.5} (2s+5) \nu_2 c_{xx}.$$

(d) 
$$Q_1 = V_1 W_1 C_1^{2s}$$
.

From (2.20), by transformation of rectangular co-ordinates, or by direct calculation, the equations of transfer in this case may readily be shown to have the form

(2.21) 
$$\frac{3(2h_0m_1)^{s+1}}{1 \cdot 3 \cdot 5 \dots (2s+3)} \Delta V_1 W_1 C_1^{2s} = \frac{2}{15} (2s+5) \nu_1 c_{yz},$$

(2.22) 
$$\frac{3(2h_0m_2)^{s+1}}{1 \cdot 3 \cdot 5 \dots (2s+3)} \Delta V_2 W_2 C_2^{2s} = \frac{2}{1 \cdot 5} (2s+5) \nu_2 c_{yz},$$

where

$$c_{yz} \equiv \frac{3}{2} \left( \frac{\partial v_0}{\partial z} + \frac{\partial w_0}{\partial y} \right).$$

(e) 
$$Q = C^{2s}$$
.

By the addition of the x, y, and z equations corresponding to (2.19), (2.20), and by changing s to s-1, we may obtain the following simple equations:—

(2.23) 
$$\frac{(2h_0m_1)^s}{1 \cdot 3 \cdot 5 \dots (2s+1)} \Delta C_1^{2s} = \nu_0 \frac{\partial \lambda'_0}{\partial t} = -\frac{(2h_0m_2)^{s+1}}{1 \cdot 3 \cdot 5 \dots (2s+1)} \Delta C_2^{2s}.$$

# § 3. The Velocity-Distribution Function.

(a) The Form of the Function.

In the uniform undisturbed state of a gas, in which  $c_0$ ,  $\lambda$ , h are constant, while  $c'_0$ ,  $h'_0$ , P are zero, the velocity-distribution functions assume Maxwell's well-known form

$$(3.01) (f_1)_0 = \left(\frac{h_0 m_1}{\pi}\right)^{3/2} e^{-h_0 m_1 C_1^2}, (f_2)_0 = \left(\frac{h_0 m_2}{\pi}\right)^{3/2} e^{-h_0 m_2 C_2^2}.$$

The suffix 0 appended to  $f_1$  and  $f_2$  is to indicate the special state to which these equations refer. They clearly satisfy the necessary conditions

(3.02) 
$$\iiint_{-\infty}^{\infty} (f_1)_0 dU_1 dV_1 dW_1 = 1, \qquad \iiint_{-\infty}^{\infty} (f_2)_0 C_1^2 dU_1 dV_1 dW_1 = \frac{3}{2h_0 m_1},$$

and similar equations with suffix 2.

In the general slightly disturbed state considered in this paper, f(U, V, W) will differ from  $(f)_0$  by an amount of the first order. From the equations of transfer (§ 2) it may be deduced\* that f may be expressed as follows:—

$$(3.03) \quad f_{1}\left(\mathsf{U}_{1},\,\mathsf{V}_{1},\,\mathsf{W}_{1}\right) = \left(f_{1}\right)_{0} \left[1 - \frac{1}{3}2h_{0}m_{1}\mathsf{A}_{0}\left(\mathsf{U}_{1}\xi'_{0} + \mathsf{V}_{1}\eta'_{0} + \mathsf{W}_{1}\xi'_{0}\right)\mathsf{F}_{1}\left(\mathsf{C}_{1}^{2}\right)\right.$$

$$\left. - \frac{1}{3}2h_{0}m_{1}\mathsf{B}_{0}\left(\mathsf{U}_{1}\frac{\partial\mathsf{T}_{0}}{\partial x} + \mathsf{V}_{1}\frac{\partial\mathsf{T}_{0}}{\partial y} + \mathsf{W}_{1}\frac{\partial\mathsf{T}_{0}}{\partial z}\right)\mathsf{G}_{1}\left(\mathsf{C}_{1}^{2}\right)\right.$$

$$\left. - \frac{2}{45}2h_{0}m_{1}\mathsf{C}_{0}\left(c_{xx}\mathsf{U}_{1}^{2} + c_{yy}\mathsf{V}_{1}^{2} + c_{zz}\mathsf{W}_{1}^{2} + 2c_{yz}\mathsf{V}_{1}\mathsf{W}_{1} + 2c_{zx}\mathsf{W}_{1}\mathsf{U}_{1} + 2c_{xy}\mathsf{U}_{1}\mathsf{V}_{1}\right)\mathsf{H}_{1}\left(\mathsf{C}_{1}^{2}\right)\right.$$

$$\left. - \mathsf{D}_{0}\frac{\partial\mathsf{X}_{0}'}{\partial t}\mathsf{J}_{1}\left(\mathsf{C}_{1}^{2}\right)\right],$$

$$\begin{split} (3^{\circ}04) \quad f_{2}\left(\cup_{2},\,\mathsf{V}_{2},\,\mathsf{W}_{2}\right) &= (f_{2})_{0} \bigg[1 - \tfrac{1}{3}2h_{0}m_{2}\mathsf{A}_{0}\left(\mathsf{U}_{2}\boldsymbol{\xi'}_{0} + \mathsf{V}_{2}\eta'_{0} + \mathsf{W}_{2}\boldsymbol{\xi'}_{0}\right)\,\mathsf{F}_{2}\left(\mathsf{C}_{2}^{\,2}\right) \\ &- \tfrac{1}{3}2\mathsf{h}_{0}m_{2}\mathsf{B}_{0}\bigg(\mathsf{U}_{2}\,\frac{\partial\mathsf{T}_{0}}{\partial x} + \mathsf{V}_{2}\,\frac{\partial\mathsf{T}_{0}}{\partial y} + \mathsf{W}_{2}\,\frac{\partial\mathsf{T}_{0}}{\partial z}\bigg)\,\mathsf{G}_{2}\left(\mathsf{C}_{2}^{\,2}\right) \\ &- \tfrac{2}{4\cdot5}2h_{0}m_{2}\mathsf{C}_{0}\left(c_{xx}\mathsf{U}_{2}^{\,2} + c_{yy}\mathsf{V}_{2}^{\,2} + c_{zz}\mathsf{W}_{2}^{\,2} + 2c_{yz}\mathsf{V}_{2}\mathsf{W}_{2} + 2c_{zx}\mathsf{W}_{2}\mathsf{U}_{2} + 2c_{zx}\mathsf{W}_{2}\mathsf{U}_{2} + 2c_{zy}\mathsf{U}_{2}\mathsf{V}_{2}\right)\,\mathsf{H}_{2}\left(\mathsf{C}_{3}^{\,2}\right) \\ &- \mathsf{D}_{0}\,\frac{\partial\lambda'_{0}}{\partial t}\,\mathsf{J}_{2}\left(\mathsf{C}_{2}^{\,2}\right)\bigg]. \end{split}$$

The constants  $A_0$ ,  $B_0$ ,  $C_0$ ,  $D_0$ , and the functions  $F(C^2)$ ,  $G(C^2)$ ,  $H(C^2)$ ,  $J(C^2)$  remain to be determined. The latter involve (x, y, z, t) only through the occurrence

<sup>\*</sup> The argument is given in my second paper, loc. cit., §§ 2, 6, and will not be repeated here.

of  $\nu$  and h (but not their derivatives) as factors. We suppose them to be capable of expansion in power series as follows\* (see Note C, p. 196):—

(3.05) 
$$F_1(C_1^2) = \sum_{r=0}^{\infty} \alpha_r \frac{(2hm_1)^r}{1 \cdot 3 \cdot 5 \dots (2r+3)} C_1^{2r}, \quad F_2(C_2^2) = \sum_{r=0}^{\infty} \alpha_{-r} \frac{(2hm_2)^r}{1 \cdot 3 \cdot 5 \dots (2r+3)} C_2^{2r},$$

(3.06) 
$$G_1(C_1^2) = \sum_{r=0}^{\infty} \beta_r \frac{(2hm_1)^r}{1 \cdot 3 \cdot 5 \dots (2r+3) r} C_1^{2r}, \quad G_2(C_2^2) = \sum_{r=0}^{\infty} \beta_{-r} \frac{(2hm_2)^r}{1 \cdot 3 \cdot 5 \dots (2r+3) r} C_2^{2r},$$

(3.07) 
$$H_1(C_1^2) = \sum_{r=0}^{\infty} \gamma_r \frac{(2hm_1)^r}{1 \cdot 3 \cdot 5 \dots (2r+5)} C_1^{2r}, \quad H_2(C_2^2) = \sum_{r=0}^{\infty} \gamma_{-r} \frac{(2hm_2)^r}{1 \cdot 3 \cdot 5 \dots (2r+5)} C_2^{2r},$$

(3.071) 
$$J_1(C_1^2) = \sum_{r=0}^{\infty} \delta_r \frac{(2hm_1)^r}{1 \cdot 3 \cdot 5 \dots (2r+1)} C_1^{2r}, \quad J_2(C_2^2) = \sum_{r=0}^{\infty} \delta_{-r} \frac{(2hm_2)^r}{1 \cdot 3 \cdot 5 \dots (2r+1)} C_2^{2r}.$$

The dash (') after the sign of summation in (3.06) is used to signify that the factor r in the denominator of the numerical coefficient is to be omitted in the first term (r=0). The choice of the notation +r and -r for the suffixes has a convenience which will become apparent later; we may remark, in passing, that for this purpose a distinction must be maintained between +0 and -0.

In (3.03) and (3.04) the constants  $A_0$ ,  $B_0$ ,  $C_0$ ,  $D_0$  can be chosen arbitrarily, but when this has been done, the remaining constants  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  all become perfectly definite.

### (b) Relations between the Coefficients.

The velocity-distribution functions f(U, V, W) must satisfy the three conditions expressed by the equations (with appropriate suffixes 1 or 2 throughout):—

(3.08) 
$$\iiint f(\mathsf{U}, \mathsf{V}, \widetilde{\mathsf{W}}) \, d\mathsf{U} \, d\mathsf{V} \, d\mathsf{W} = 1,$$

(3.09) 
$$\iiint f(\mathsf{U}, \mathsf{V}, \mathsf{W}) \, \mathrm{C}^2 \, d\mathsf{U} \, d\mathsf{V} \, d\mathsf{W} = \frac{3}{2hm}$$
  $(h_1 \text{ or } h_2),$ 

(3.10) 
$$\iiint f_1(U_1, V_1, W_1) \cup_1 d \cup_1 d V_1 d W_1 = u_1 - u_0 = u'_0 / \lambda_1,$$
$$\iiint f_2(U_2, V_2, W_2) \cup_2 d \cup_2 d V_2 d W_2 = u_2 - u_0 = -u'_0 / \lambda_2.$$

<sup>\* [</sup>Here, and throughout the remainder of the paper, where h and T appear without any suffix, they are to be read as  $h_0$  and  $T_0$ .—June 2, 1916.]

These yield the equations

$$\sum_{0}^{\infty} \delta_{r} = 0,$$

(3.102) 
$$\sum_{0}^{\infty} \delta_{-r} = 0.$$

(3.103) 
$$\frac{1}{3} D_0 \frac{\partial \lambda'_0}{\partial t} \sum_{n=0}^{\infty} (2r+3) \, \delta_r = -\frac{T'_0}{\lambda_1 T_0},$$

(3.104) 
$$\frac{1}{3} \mathcal{D}_0 \frac{\partial \lambda'_0}{\partial t} \sum_{0}^{\infty} (2r+3) \, \delta_{-r} = \frac{\mathcal{T}'_0}{\lambda_2 \mathcal{T}_0}.$$

$$(3.11) -\frac{1}{9}\left\{A_0 \xi'_0 \sum_{0}^{\infty} \alpha_r + B_0 \frac{\partial T}{\partial x} \sum_{0}^{\infty} r^{-1} \beta_r\right\} = u'_0 / \lambda_1,$$

(3.12) 
$$-\frac{1}{9} \left\{ A_0 \xi'_0 \sum_{0}^{\infty} \alpha_{-r} + B_0 \frac{\partial T}{\partial x} \sum_{0}^{\infty'} r^{-1} \beta_{-r} \right\} = -u'_0 / \lambda_2.$$

In each of the pairs (3·103)–(3·12) we will multiply the first equation by  $\lambda_1$  and the second by  $\lambda_2$  respectively, and add. We may separately equate the coefficients of  $\xi'_0$  and  $\frac{\partial T}{\partial x}$  (in the second resulting equation) to zero, since these quantities are quite independent of one another, and of their coefficients. We thus obtain the conditions

(3.121) 
$$\lambda_{1} \sum_{0}^{\infty} (2r+3) \, \delta_{r} = -\delta_{0}' = -\lambda_{2} \sum_{0}^{\infty} (2r+3) \, \delta_{-r},$$

or, by (3.101), (3.102),

$$\lambda_1 \sum_{0}^{\infty} \alpha_r = -\alpha'_0 = -\lambda_2 \sum_{0}^{\infty} \alpha_{-r},$$

(3.14) 
$$\lambda_1 \sum_{0}^{\infty} r^{-1} \beta_r = -\beta_0' = -\lambda_2 \sum_{0}^{\infty} r^{-1} \beta_{-r},$$

where also we have introduced a convenient notation for the separate sums involved. Expressed in terms of this (3.101)–(3.12) are equivalent to

(3.15) 
$$u_0' = \frac{1}{9} \left( \alpha_0' A_0 \hat{\xi}_0' + \beta_0' B_0 \frac{\partial T}{\partial x} \right),$$

(3.151) 
$$T_0' = \frac{1}{3} D_0 T_0 \delta_0' \frac{\partial \lambda_0'}{\partial t}$$

[Throughout the remainder of the paper we shall neglect  $\frac{\delta \lambda'_0}{\delta t}$ , i.e., we shall practically assume that the ratio of mixture is not varying with respect to time. The values

of  $\alpha$ ,  $\beta$ ,  $\gamma$  determined in the succeeding sections will, however, hold good also in the general case; the determination of the  $\delta$ 's will be found in the Appendix. All the corrections to  $(f)_0$  are of the first order, and hence are separately deducible; the complete value is obtained by adding to the series in  $\alpha$ ,  $\beta$ ,  $\gamma$ , calculated in the body of the paper, the series in  $\delta$ , determined in the Appendix.—June 2, 1916.]

## § 4. Completion of the Equations of Transfer.

(a) The Values of 
$$\Delta Q$$
.

We may now complete the equations of transfer (2.07)–(2.10) by the insertion of the values of  $\Delta Q$ , calculated in terms of the constants in the expressions for f(U, V, W) given in § 3. The calculation of  $\Delta Q$  is a lengthy and elaborate operation which will not be described here, since a full account of it is to be found in my second memoir ('Phil. Trans.,' A, vol. 216, § 7, p. 301). It appears that only those terms in f which are of odd degree in U, V, W contribute to the resulting expression for  $\Delta UC^{2s}$ , and only the even terms, similarly, contribute to  $\Delta U^2C^{2s}$ . The following results will be quoted forthwith:—

$$(4.01) \frac{3(2hm_{1})^{s}}{2^{s+1}(s+\frac{3}{2})_{s+1}} m_{1}\Delta \cup_{1} C_{1}^{2s} = \sum_{r=0}^{\infty} \left[ m_{1} \left( N_{rs} A_{0} \xi'_{0} \alpha_{r} + s N'_{rs} B_{0} \frac{\partial T}{\partial x} \beta_{r} \right) \left\{ \rho_{11}(r_{1}s_{1}) + \rho_{12}(r_{1}s_{1}) \right\} + m_{2} \left( N_{rs} A_{0} \xi'_{0} \alpha_{-r} + s N'_{rs} B_{0} \frac{\partial T}{\partial x} \beta_{-r} \right) \rho_{12}(r_{2}s_{1}) \right],$$

$$(4.02) \frac{3(2hm_{2})^{s}}{2^{s+1}(s+\frac{3}{2})_{s+1}} m_{2}\Delta \cup_{2} C_{2}^{2s} = \sum_{r=0}^{\infty} \left[ m_{1} \left( N_{rs} A_{0} \xi'_{0} \alpha_{r} + s N'_{rs} B_{0} \frac{\partial T}{\partial x} \beta_{r} \right) \rho_{21} (r_{1}s_{2}) + m_{2} \left( N_{rs} A_{0} \xi'_{0} \alpha_{-r} + s N'_{rs} B_{0} \frac{\partial T}{\partial x} \beta_{-r} \right) \left\{ \rho_{22} (r_{2}s_{2}) + \rho_{21} (r_{2}s_{2}) \right\} \right],$$

$$(4.03) \quad \frac{45 \left(2 h m_1\right)^{s+1}}{2^{s+2} \left(s+\frac{5}{2}\right)_{s+2}} \frac{1}{2 \nu_1} \Delta \mathsf{U}_1^{\ 2} \mathsf{C}_1^{\ 2s} = \frac{1}{\nu_1} \mathsf{C}_0 c_{xx} \sum_{r=0}^{\infty} \mathsf{N}''_{rs} \left[ \gamma_r \left\{ \rho'_{11}(r_1 s_1) + \rho'_{12}(r_1 s_1) \right\} \right. \\ \left. + \gamma_{-r} \rho'_{12}(r_2 s_1) \right],$$

$$(4.04) \quad \frac{45 \, (2hm_2)^{s+1}}{2^{s+2} \, (s+\frac{5}{2})_{s+2}} \frac{1}{2\nu_2} \Delta \, \mathsf{U}_2{}^2 \mathsf{C}_2{}^{2s} = \frac{1}{\nu_2} \mathsf{C}_0 c_{xx} \sum_{r=0}^{\infty} \mathsf{N''}_{rs} \big[ \gamma_r \rho'_{21}(r_1 s_2) + \gamma_{-r} \big\{ \rho'_{22}(r_2 s_2) + \rho'_{21}(r_2 s_2) \big\} \big].$$

#### (b) Explanation of the Notation.

In the above equations r and s may take all positive integral values, including zero. We shall presently alter our notation so as to consider also negative integral values, but in the following definitions of  $N_{rs}$ ,  $N'_{rs}$ ,  $N''_{rs}$ , the positive numerical values of r and s are in every case to be used on the right-hand side:

(4.05) 
$$N_{rs} = \{2^{r+s+2}(r+\frac{3}{2})_{r+1}(s+\frac{3}{2})_{s+1}\}^{-1}, \qquad N'_{rs} = \frac{1}{rs}N_{rs}, \qquad N''_{rs} = N_{r+1,s+1}.$$

In the case of  $N'_{rs}$ , the factor r is to be omitted from the denominator when r = 0; when s = 0, the value of  $sN'_{rs}$ , in which form  $N'_{rs}$  occurs in (4.01), (4.02), is to be taken VOL. CCXVII.—A.

as  $r^{-1}N_{rs}$ . The meaning of the symbols  $(r+\frac{3}{2})_{r+1}$ ,  $(s+\frac{3}{2})_{s+1}$  will be understood from the following definition, where q is a positive integer and p any number whatsoever:

(4.06) 
$$p_q \equiv p(p-1)(p-2)\dots(p-q+1), \qquad p_0 = 1.$$

We shall have frequent occasion to use this factorial symbol.

The following are the expressions found for  $\rho(rs)$  and  $\rho'(rs)$  in the various cases:—

cases: 
$$\begin{array}{ll} \text{(4'07)} & \rho_{11}\left(r_{1}s_{1}\right) = \frac{3}{3}^{2}v_{1}^{2} \int \int e^{-(x^{2}+y^{2})}x^{2}y^{2} \\ & \sum_{k=1}^{3(r+1,s+1)} \phi_{11}^{2k}(y) \bigg[ B^{2k}(r+1,s) + B^{2k}(r,s+1) \\ & + 2y^{2} \bigg\{ \frac{2k+1}{4k+1} B^{2k+1}(r,s) + \frac{2k}{4k+1} B^{2k-1}(r,s) - B^{2k}(r,s) \bigg\} \bigg] dx \, dy, \\ \text{(4'08)} & \rho_{12}\left(r_{1}s_{1}\right) = \frac{1}{3}^{6}v_{1}v_{2} \int \int e^{-(x^{2}+y^{2})}x^{2}y^{2} \\ & \sum_{k=0}^{(r+1,s+1)} \left[ \phi_{12}^{k}(y) \left\{ B^{k}(r+1,s) + B^{k}(r,s+1) \right\} \\ & + 4\mu_{2}y^{2}\psi_{12}^{k}(y) B^{k}\left(r,s\right) \right]_{1212} dx \, dy. \\ \text{(4'09)} & \rho_{12}\left(r_{2}s_{1}\right) = \frac{1}{3}^{6}v_{1}v_{2}\mu_{12}^{y_{1}} \int \int e^{-(x^{2}+y^{2})}x^{2}y^{2} \\ & \sum_{k=1}^{(r+1,s+1)} \left( -1 \right)^{k} \left[ \phi_{12}^{k}(y) \left\{ \mu_{12}^{y_{1}} B^{k}\left(r+1,s\right) - 2\left(\mu_{1}\mu_{2}\right)^{-y_{1}}y^{2}B^{k}\left(r,s\right) \right. \\ & + \mu_{21}^{y_{1}} B^{k}\left(r,s+1\right) \right\} - 4\left(\mu_{1}\mu_{2}\right)^{y_{2}}y^{2}\psi_{12}^{k}(y) B^{k}\left(r,s\right) \right]_{2112} dx \, dy. \\ \text{(4'10)} & \rho_{11}^{\prime}\left(r_{1}s_{1}\right) = \frac{1}{6}^{6}v_{1}^{2} \int \int e^{-(x^{2}+y^{2})}x^{2}y^{2} \\ & \sum_{k=1}^{3(r+2,s+2)} \phi_{11}^{2k}\left(y\right) \left[ B^{2k}\left(r+2,s\right) + \frac{2}{3}B^{2k}\left(r+1,s+1\right) + B^{2k}\left(r,s+2\right) \\ & + 4y^{2} \left\{ \frac{2k+1}{4k+1} \left( B^{2k+1}\left(r+1,s\right) + B^{2k+1}\left(r,s+1\right) \right) \right. \\ & + \left. \frac{2k}{4k+1} \left( B^{2k-1}\left(r+1,s\right) + B^{2k}\left(r,s+1\right) \right) \right\} \\ & + 4y^{4} \left\{ \frac{(2k+2)\left(2k+1\right)}{\left(4k+3\right)\left(4k+1\right)} B^{2k+2}\left(r,s\right) \\ & + \left( \frac{(2k+1)^{2}}{\left(4k+3\right)\left(4k+1\right)} + \frac{(2k)^{2}}{\left(4k+1\right)\left(4k-1\right)} + 1 \right) B^{2k}\left(r,s\right) \end{array} \right.$$

 $+\frac{2k(2k-1)}{(4k+1)(4k-1)}B^{2k-2}(r,s)$ 

 $-2\left(\frac{2k+1}{4k+1}B^{2k+1}(r,s)+\frac{2k}{4k+1}B^{2k-1}(r,s)\right)\right]dx\,dy.$ 

$$(4.11) \quad \rho'_{12}(r_{1}s_{1}) = \frac{8}{5}\nu_{1}\nu_{2} \iint e^{-(x^{2}+y^{3})}x^{2}y^{2}$$

$$\sum_{k=0}^{(r+2, s+2)} \left[\phi_{12}^{k}(y)\left\{B^{k}(r+2, s) + \frac{2}{3}B^{k}(r+1, s+1) + B^{k}(r, s+2)\right\} + 8\mu_{2}y^{2}\psi_{12}^{k}(y)\left\{B^{k}(r+1, s) + B^{k}(r, s+1)\right\} - 16\mu_{2}^{2}y^{4}\chi_{12}^{k}(y)B^{k}(r, s)\right]_{1212}dxdy.$$

$$(4.12) \quad \rho'_{12}(r_{2}s_{1}) = \frac{8}{5}\nu_{1}\nu_{2} \iint e^{-(x^{2}+y^{2})}x^{2}y^{2}$$

$$\sum_{k=0}^{(r+2, s+2)} (-1)^{k} \left[\phi_{12}^{k}(y) \left\{\mu_{12}B^{k}(r+2, s) + \frac{2}{3}B^{k}(r+1, s+1) + \mu_{21}B^{k}(r, s+2) - 4\left(\mu_{1}\mu_{2}\right)^{-1/2}y^{2}\left(\mu_{12}^{-1/2}B^{k}(r+1, s) + \mu_{21}^{-1/2}B^{k}(r, s+1)\right) + 4\mu_{1}\mu_{2}y^{4}B^{k}(r, s)\right\} - 8\left(\mu_{1}\mu_{2}\right)^{1/2}y^{2}\psi_{12}^{k}(y)\left\{\mu_{12}^{-1/2}B^{k}(r+1, s) - 2\left(\mu_{1}\mu_{2}\right)^{-1/2}y^{2}B^{k}(r, s) + \mu_{21}^{-1/2}B^{k}(r, s+1)\right\} - 16\mu_{1}\mu_{2}y^{4}\chi_{12}^{k}(y)B^{k}(r, s)\right]_{2112}dxdy.$$

There are also six other equations, similar to the above, except that the suffixes 1 and 2 are interchanged; these need not be written down here.

The limits of integration of x and y throughout the above expressions are 0 and  $\infty$ . The upper limits of the summations are in each case indicated by two numbers, which are not necessarily integers; the upper limit is to be taken equal to the greatest integer which does not exceed either of these two numbers. The suffixes 1212 or 2112 on the right-hand of the main square brackets of (4.08), (4.09), (4.11), (4.12) are there placed only for convenience in printing: they should really be appended to each of the symbols  $B^k(m, n)$  contained within the brackets. These symbols are defined by the following equations:—

(4.13) 
$$B^{k}_{1212}(m,n) = {}^{m}A^{k}(2\mu_{1}x^{2}, 2\mu_{2}y^{2}) \cdot {}^{n}A^{k}(2\mu_{1}x^{2}, 2\mu_{2}y^{2}),$$

$$B^{k}_{2112}(m,n) = {}^{m}A^{k}(2\mu_{2}x^{2}, 2\mu_{1}y^{2}) \cdot {}^{n}A^{k}(2\mu_{1}x^{2}, 2\mu_{2}y^{2}), \quad B^{k}(m,n) = {}^{m}A^{k}(x^{2}, y^{2}) \, {}^{n}A^{k}(x^{2}, y^{2}),$$

where  ${}^{m}A^{k}(u, v)$  is a polynomial in powers of u, v defined thus:—

$$(4.14) {}^{m}A^{k}(u,v) = {}^{m}A^{k}(v,u) = \left(\frac{u}{v}\right)^{1/2k} \sum_{t=k}^{m} \frac{m_{t}}{(t+\frac{1}{2})_{t}} \frac{(m+\frac{1}{2})_{t-k}}{(t-k)!} u^{m-t}v^{t} k \leqslant m.$$

When k > m,  ${}^{m}A^{k}(u, v)$  is zero. Also  $\mu_{1}, \mu_{2}, \mu_{12}, \mu_{21}$ , have the following values:—

(4.15) 
$$\mu_1 = m_1/(m_1 + m_2)$$
,  $\mu_2 = m_2/(m_1 + m_2)$ ,  $\mu_{12} = m_1/m_2 = \mu_1/\mu_2$ ,  $\mu_{21} = m_2/m_1 = \mu_2/\mu_1$ , so that

(4.16) 
$$\mu_1 + \mu_2 = 1, \qquad \mu_{12}\mu_{21} = 1.$$
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Finally we must define the functions  $\phi^k(y)$ ,  $\psi^k(y)$ ,  $\chi^k(y)$ ; these are the only quantities in the expressions for  $\rho(r,s)$  and  $\rho'(r,s)$  which depend on the law of interaction between molecules. If two molecules  $m_1$ ,  $m_2$  encounter one another, the direction of their relative velocity will be changed through a certain angle  $\theta_{12}$  in a plane parallel to the initial relative velocity and to the perpendicular (of length p) between their initial and final lines of undisturbed rectilinear motion; denoting the magnitude of the initial or final relative velocity by  $\left(\frac{m_1+m_2}{hm_1m_2}\right)^{l/2}y$ ,  $\theta_{12}$  will be a function of p and p, the nature of the function being determined by the mode of interaction between molecules in proximity to one another. Then we have

$$(4.17) \phi_{12}^{k}(y) = (2k+1) \{ \mu_{1}\mu_{2}h(m_{1}+m_{2}) \}^{-1/2}y \int_{0}^{\infty} \{ 1 - P_{k}(\cos \theta_{12}) \} p dp,$$

$$(4.18) \qquad \psi_{12}{}^{k}(y) = (2k+1) \left\{ \mu_{1}\mu_{2}h\left(m_{1}+m_{2}\right)\right\}^{-1/2} y \int_{0}^{\infty} (1-\cos\,\theta_{12}) \mathrm{P}_{k}(\cos\,\theta_{12}) \, p \, dp,$$

(4.19) 
$$\chi_{12}^{k}(y) = (2k+1) \{ \mu_1 \mu_2 h(m_1 + m_2) \}^{-1/2} y \int_0^\infty (1 - \cos \theta_{12})^2 P_k(\cos \theta_{12}) p \, dp,$$

where  $P_k(\cos \theta_{12})$  denotes, as usual, the Legendre function of  $\cos \theta_{12}$  of order k. By changing the suffix 1 or 2 throughout into 2 or 1 respectively, we obtain the corresponding expressions for  $\phi_{22}^{k}$  or  $\phi_{11}^{k}$ , and so on; mere interchange of the suffixes does not affect the functions.

By means of the recurrence formula for the Legendre functions, viz.,

$$(4.20) (k+1) P_{k+1} - (2k+1) \cos \theta_{12} P_k + k P_{k-1} = 0,$$

we may express  $\psi$  and  $\chi$  in terms of the function  $\phi$ . Thus for  $\psi^{k}(y)$  we have

(4.21) 
$$\psi^{k}(y) = \frac{k+1}{2k+3} \phi^{k+1}(y) - \phi^{k}(y) + \frac{k}{2k-1} \phi^{k-1}(y).$$

In this way we may prove that

$$(4\cdot22) \quad \psi^{\scriptscriptstyle 0}(y) = \frac{1}{3}\phi^{\scriptscriptstyle 1}(y), \quad \chi^{\scriptscriptstyle 0}(y) = \frac{2}{3}\phi^{\scriptscriptstyle 1}(y) - \frac{2}{15}\phi^{\scriptscriptstyle 2}(y), \quad \psi^{\scriptscriptstyle 1}(y) = -\phi^{\scriptscriptstyle 1}(y) + \frac{2}{5}\phi^{\scriptscriptstyle 2}(y).$$

From the symmetry, with respect to r and s, of the expressions on the right hand of equations (4.07), (4.08), (4.10), (4.11) it is clear that

$$(4.23) \quad \rho_{11}(r_1s_1) = \rho_{11}(s_1r_1), \quad \rho'_{11}(r_1s_1) = \rho'_{11}(s_1r_1), \quad \rho_{12}(r_1s_1) = \rho_{12}(s_1r_1), \quad \rho'_{12}(r_1s_1) = \rho'_{12}(s_1r_1).$$

$$(c) \quad Special \ Values \ of \ \rho(r, s) \ and \ \rho'(r, s).$$

To facilitate the exposition of subsequent parts of the work it is convenient at this stage to write down certain special cases of the equations (4.07)–(4.12), after executing the integrations with respect to x and y. Owing to the generality of the functions

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 $\phi$ ,  $\psi$ ,  $\chi$  (depending on the functional relation between  $\theta_{12}$  and p, y) the integration with respect to y can only be made *formally*, however, and for this purpose we shall use the notation

(4.24) 
$$K^{k}(t) \equiv \frac{4\pi^{-1/2}}{(t+k+\frac{1}{2})_{t+k}} \int_{0}^{\infty} e^{-y^{2}} \phi^{k}(y) y^{2(t+k-1)} dy.$$

The suffix 11, 12, or 22 is to be appended to  $K^k(t)$  to correspond with the suffix of  $\phi^k(y)$  on the right. The notation is chosen so as to make  $K^k(t)$  equal to  $\phi^k(y)$  when this is independent of y, as in the case of molecules which obey Maxwell's fifth-power law.\*

For small values of r and s it is convenient to simplify our formulæ by writing also

$$(4.25) k_t \equiv \frac{\mathrm{K'}_{12}\left(t\right)}{\mathrm{K'}_{12}\left(0\right)}, k_{11}^t \equiv \frac{\mathrm{K'}_{11}\left(t\right)}{\mathrm{K'}_{12}\left(0\right)}, k_{12}^t \equiv \frac{\mathrm{K'}_{12}\left(t\right)}{\mathrm{K'}_{12}\left(0\right)}, k_{22}^t \equiv \frac{\mathrm{K'}_{22}\left(t\right)}{\mathrm{K'}_{12}\left(0\right)}.$$

In terms of the above notation we may now give the following results:—

(4.26) 
$$\rho_{11}(r_10_1) = \rho_{11}(0_1s_1) = 0$$
,  $\rho_{11}(s_11_1) = \rho_{11}(1_1s_1) = \frac{1}{4}\frac{6}{5}\pi\nu_1^2s(s+\frac{3}{2})_{s+1}K'_{12}(0)\sum_{0=s-1}^{s-1}C_tk^t_{11}$ ,

(4.27) 
$$\rho_{12}(s_10_1) = \rho_{12}(0_1s_1) = \frac{4}{9}\pi\nu_1\nu_2\mu_22^s(s+\frac{3}{2})_{s+1} K'_{12}(0) \sum_{0}^{s} C_t\mu_1^{s-t}\mu_2^t k_t,$$

(4.28) 
$$\rho_{12}(r_20_1) = -\frac{4}{9}\pi\nu_1\nu_2\mu_12^r(r+\frac{3}{2})_{r+1} K'_{12}(0) \sum_{0}^{r} C_t\mu_2^{r-t}\mu_1^t k_t,$$

(4.29) 
$$\rho_{12}(0_2s_1) = -\frac{4}{9}\pi\nu_1\nu_2\mu_1 2^s \left(s + \frac{3}{2}\right)_{s+1} K'_{12}(0) \sum_{s=0}^{s} C_t \mu_1^{s-t} \mu_2^{t} k_t,$$

$$(4.30) \quad \rho_{12}(s_1 1_1) = \rho_{12}(1_1 s_1) = \frac{8}{9} \pi \nu_1 \nu_2 \mu_2 2^s (s + \frac{3}{2})_{s+1} K'_{12}(0) \left[ \frac{5}{2} \sum_{0}^{s} C_t \mu_1^{s-t} \mu_2^{t} (\mu_1 k_t + \mu_2 k_{t+1}) + s \sum_{0}^{s-1} C_t \mu_1^{s-1-t} \mu_2^{t} (3\mu_1^{s} k_t + \mu_2^{s} k_{t+2} + \frac{4}{5} \mu_1 \mu_2 k_{12}^{t}) \right],$$

$$(4.31) \quad \rho_{12}(1_{2}s_{1}) = -\frac{8}{9}\pi\nu_{1}\nu_{2}\mu_{1}2^{s}(s+\frac{3}{2})_{s+1}K'_{12}(0)\left[\frac{5}{2}\sum_{0}^{s}C_{t}\mu_{1}^{s-t}\mu_{2}^{t}(\mu_{2}k_{t}+\mu_{1}k_{t+1})\right. \\ \left. + s\mu_{1}\mu_{2}\sum_{0}^{s-1}C_{t}\mu_{1}^{s-1-t}\mu_{2}^{t}(3k_{t}+k_{t+2}-\frac{4}{5}k_{12}^{t})\right],$$

(4.32) 
$$\rho'_{11}(0_1s_1) = \rho'_{11}(s_10_1) = \frac{8}{75}\pi\nu_1^2(s+\frac{5}{2})_{s+2} K'_{12}(0) \sum_{s}^{s} C_t k^t_{11},$$

(4.33) 
$$\rho'_{12}(0_1s_1) = \rho'_{12}(s_10_1) = \frac{3}{4}\frac{2}{5}\pi\nu_1\nu_2\mu_2 2^s \left(s + \frac{5}{2}\right)_{s+2} K'_{12}(0) \sum_{0}^{s} C_t \mu_1^{s-t} \mu_2^{t} \left(\mu_1 k_t + \frac{3}{10}\mu_2 k_{12}^{t}\right),$$

(4.34) 
$$\rho'_{12}(0_2s_1) = \frac{32}{45}\pi\nu_1\nu_2\mu_2 2^s \left(s + \frac{5}{2}\right)_{s+2} K'_{12}(0) \sum_{0}^{s} C_t \mu_1^{s-t} \mu_2^{t} \left(-\mu_1 k_t + \frac{3}{10}\mu_1 k_{12}^{t}\right).$$

<sup>\*</sup> Cf. 'Phil. Trans.,' A, vol. 216, § 9 (C), p. 323.

It may readily be deduced from the above equations that

(4.35) 
$$\rho_{12}(r_10_1) = -\rho_{21}(r_10_2), \quad \rho_{12}(r_20_1) = -\rho_{21}(r_20_2),$$

(4.36) 
$$\mu_1 \rho_{12} (0_1 s_1) = -\mu_2 \rho_{12} (0_2 s_1), \quad \mu_1 \rho_{21} (0_1 s_2) = -\mu_2 \rho_{21} (0_2 s_2).$$

Also, in the case of Maxwellian molecules, for which  $k_t = 1$  and  $k_{12}^t = k_{12}^0$  (whatever the value of t) we shall have

$$(4.37) \qquad \rho_{12}(1_1s_1) - 5\rho_{12}(0_1s_1) = \frac{8}{9}\pi\nu_1\nu_2\mu_2 2^s s \left(s + \frac{3}{2}\right)_{s+1} K'_{12}(0) \left(3\mu_1^2 + \mu_2^2 + \frac{4}{5}\mu_1\mu_2 k^0_{12}\right),$$

$$(4.38) \qquad \rho_{12}(1_2s_1) - 5\rho_{12}(0_2s_1) = -\frac{8}{9}\pi\nu_1\nu_2\mu_1\mu_2^2 2^s s \left(s + \frac{3}{2}\right)_{s+1} K'_{12}(0) \left(4 + \frac{4}{5}k^0_{12}\right).$$

§ 5. The Symbolic Solution for the Coefficients in f(U, V, W).

(a) The Linear Equations for 
$$\alpha$$
,  $\beta$ ,  $\gamma$ .

We now refer back to the two corresponding sets of equations (2.07)-(2.10) and (4.01)-(4.04). For the two members of each pair of corresponding equations the left-hand side is the same, so that we may equate the right-hand sides. Also, as regards the first two pairs, we may separately equate the parts which contain as factors the independent quantities  $\xi'_0$  and  $\frac{\partial T}{\partial x}$ . Thus we have

$$(5.01) \quad \frac{1}{\nu_0} A_0 \sum_{r=0}^{\infty} N_{rs} \left[ m_1 \alpha_r \left\{ \rho_{11} \left( r_1 s_1 \right) + \rho_{12} \left( r_1 s_1 \right) \right\} + m_2 \alpha_{-r} \rho_{12} \left( r_2 s_1 \right) \right] = 1, \quad (s = 0 \text{ to } s = \infty),$$

$$(5.02) - \frac{1}{\nu_0} A_0 \sum_{r=0}^{\infty} N_{rs} [m_1 \alpha_r \rho_{21}(r_1 s_2) + m_2 \alpha_{-r} \{ \rho_{22}(r_2 s_2) + \rho_{21}(r_2 s_2) \}] = 1, \quad (s = 0 \text{ to } s = \infty),$$

$$(5.03) \quad \frac{1}{\mathrm{R}\nu_1} \, \mathrm{B}_0 \, \sum_{r=0}^{\infty} \mathrm{N}'_{rs} \big[ m_1 \beta_r \{ \rho_{11}(r_1 s_1) + \rho_{12}(r_1 s_1) \} + m_2 \beta_{-r} \rho_{12}(r_2 s_1) \big] = 1, \quad (s=1 \text{ to } s=\infty),$$

$$(5.04) \quad \frac{1}{\mathrm{R}\nu_2} \, \mathrm{B}_0 \, \sum_{r=0}^{\infty} \mathrm{N}'_{rs} \big[ m_1 \beta_r \rho_{21}(r_1 s_2) + m_2 \beta_{-r} \{ \rho_{22}(r_2 s_2) + \rho_{21}(r_2 s_2) \} \big] = 1, \quad (s = 1 \text{ to } s = \infty),$$

(5.05) 
$$\frac{1}{\mathrm{R}\nu_0} \, \mathrm{B}_0 \, \sum_{r=0}^{\infty} s \mathrm{N}'_{rs} \left[ m_1 \beta_r \rho_{12} \left( r_1 s_1 \right) + m_2 \beta_{-r} \rho_{12} \left( r_2 s_1 \right) \right] = 0, \quad (s=0),$$

(5.06) 
$$\frac{1}{\nu_1} C_0 \sum_{r=0}^{\infty} N''_{rs} \left[ \gamma_r \left\{ \rho'_{11} \left( r_1 s_1 \right) + \rho'_{12} \left( r_1 s_1 \right) \right\} + \gamma_{-r} \rho'_{12} \left( r_2 s_1 \right) \right\} \right] = 1, \quad (s = 0 \text{ to } s = \infty),$$

$$(5.07) \quad \frac{1}{\nu_2} C_0 \sum_{r=0}^{\infty} N''_{rs} \left[ \gamma_r \rho'_{21} \left( r_1 s_2 \right) + \gamma_{-r} \left\{ \rho'_{22} \left( r_2 s_2 \right) + \rho'_{21} \left( r_2 s_2 \right) \right\} \right] = 1, \quad (s = 0 \text{ to } s = \infty).$$

By virtue of (4.26) and (4.35) the equations (5.01) and (5.02) are identical when s = 0, while (5.03) and (5.04) then assume the same special form (5.05); we may

recall that in § 4 (b) the value of  $sN'_{rs}$  was defined to be  $r^{-1}N_{rs}$  when s = 0 (or  $N_{rs}$  when r is also zero). Moreover, from (4.26) and (4.36), it is clear that in (5.01)-(5.05) the ratio of the factors of  $\alpha_0$  and  $\alpha_{-0}$ , or of  $\beta_0$  and  $\beta_{-0}$  has the constant value -1. Consequently, the above equations do not enable us to determine the separate values of  $\alpha_0$  and  $\alpha_{-0}$ , or  $\beta_0$  and  $\beta_{-0}$ , but only of  $\alpha_0 - \alpha_{-0}$  and  $\beta_0 - \beta_{-0}$ , which form single unknowns. When these and all the other values of  $\alpha_r$  and  $\beta_r$  ( $r \neq 0$ ) have been determined, the separate coefficients  $\alpha_0$ ,  $\alpha_{-0}$ ,  $\beta_0$ ,  $\beta_{-0}$  may be deduced with the aid of (3.13) and (3.14).

In order to simplify the notation of our formal solutions for the coefficients  $\alpha$ ,  $\beta$ ,  $\gamma$ , it is convenient to re-write (5.01)-(5.07) in the form

(5.08) 
$$\sum_{r=-\infty}^{-1} a_{rs} \alpha_r + a_{0s} (\alpha_0 - \alpha_{-0}) + \sum_{r=1}^{\infty} a_{rs} \alpha_r = 1 \quad (s = -\infty \text{ to } s = \infty, \text{ including } s = 0),$$

(5.09) 
$$\sum_{r=-\infty}^{-1} b_{r+1,s+1} \beta_r - b_s \frac{\beta'_0}{\lambda_1 \lambda_2} + \sum_{r=1}^{\infty} b_{r-1,s-1} \beta_r = 1 \quad (s = -\infty \text{ to } s = \infty, \text{ excluding } s = 0),$$

(5.10) 
$$\sum_{r=-\infty}^{-1} b_{r+1} \beta_r - b \frac{\beta'_0}{\lambda_1 \lambda_2} + \sum_{r=1}^{\infty} b_{r-1} \beta_r = 0,$$

(5.11) 
$$\sum_{r=-\infty}^{\infty} c_{rs} \gamma_r = 1 \quad (\pm r, \pm s \text{ range from 0 to } \infty).$$

In obtaining (5.09), (5.10) from (5.03)–(5.05) we have eliminated  $\beta_0$  and  $\beta_{-0}$  by means of (3.14), and in order to preserve symmetry we have subtracted  $1/s\lambda_1$  or  $1/s\lambda_2$  times the equation (5.05) from (5.03) or (5.04) respectively. The new symbols are defined as follows:—

(5.12) 
$$s \geqslant 0$$
  $a_{0s} = -a_{-0s} = \frac{m_1}{\nu_0} A_0 N_{0s} \rho_{12}(0_1 s_1), \quad a_{rs} = \frac{m_1}{\nu_0} A_0 N_{rs} \{ \rho_{11}(r_1 s_1) + \rho_{12}(r_1 s_1) \} \quad r > 0,$ 

(5.13) 
$$s \leqslant 0$$
  $\alpha_{0s} = -\alpha_{-0s} = -\frac{m_1}{\nu_0} A_0 N_{0s} \rho_{21}(0_1 s_2), \ \alpha_{rs} = -\frac{m_2}{\nu_0} A_0 N_{rs} \{ \rho_{22}(r_2 s_2) + \rho_{21}(r_2 s_2) \} \ r < 0,$ 

(5.14) 
$$r < 0, s > 0$$
  $a_{rs} = \frac{m_2}{\nu_0} A_0 N_{rs} \rho_{12}(r_2 s_1), \quad a_{rs} = -\frac{m_1}{\nu_0} A_0 N_{rs} \rho_{21}(r_1 s_2) \quad r > 0, s \le 0,$ 

(5.15) 
$$r \geqslant 0$$
  $b_r = \frac{B_0}{A_0 R} \frac{1}{r+1} (a_{r+1,0} - a_{00}), b = \frac{B_0}{A_0 R} a_{00}, b_r = \frac{B_0}{A_0 R} \frac{1}{r+1} (a_{r-1,0} - a_{-00}) r \leqslant -0,$ 

$$(5.16) \quad s \geqslant 0 \quad b_s = \frac{1}{\lambda_1} \frac{B_0}{A_0 R} \frac{1}{s+1} (\alpha_{0,s+1} - \alpha_{00}), \quad b_s = -\frac{1}{\lambda_2} \frac{B_0}{A_0 R} \frac{1}{s+1} (\alpha_{0,s-1} - \alpha_{00}) \quad s \leqslant -0,$$

$$\begin{cases} b_{rs} = \frac{1}{\lambda_1} \frac{B_0}{A_0 R} \frac{1}{(r+1)(s+1)} \{a_{r+1,s+1} - a_{0,s+1} - a_{r+1,0} + a_{00}\} & r \geqslant 0, \\ b_{rs} = \frac{1}{\lambda_1} \frac{B_0}{A_0 R} \frac{1}{(r+1)(s+1)} \{a_{r-1,s+1} - a_{-0,s+1} - a_{r-1,0} + a_{-00}\} & r \leqslant -0, \end{cases}$$

$$(5.18) \ s \leqslant -0 \ \begin{cases} b_{rs} = -\frac{1}{\lambda_2} \frac{B_0}{A_0 R} \frac{1}{(r+1)(s+1)} \{a_{r+1, s-1} - a_{0, s-1} - a_{r+1, 0} + a_{00}\} & r \geqslant 0, \\ b_{rs} = -\frac{1}{\lambda_2} \frac{B_0}{A_0 R} \frac{1}{(r+1)(s+1)} \{a_{r-1, s-1} - a_{-0, s-1} - a_{r-1, 0} + a_{-00}\} & r \leqslant -0 \end{cases}$$

(5.19) 
$$r \geqslant 0, s \geqslant 0$$
  $c_{rs} = \frac{1}{\nu_1} C_0 N''_{rs} \{ \rho'_{11} (r_1 s_1) + \rho'_{12} (r_1 s_1) \}$  
$$c_{rs} = \frac{1}{\nu_1} C_0 N''_{rs} \rho'_{12} (r_2 s_1) \quad r \leqslant -0, s \geqslant 0,$$

(5.20) 
$$r \leqslant -0, s \leqslant -0$$
  $c_{rs} = \frac{1}{\nu_2} C_0 N''_{rs} \{ \rho'_{22} (r_2 s_2) + \rho'_{2f} (r_2 s_2) \}$ 

$$c_{rs} = \frac{1}{\nu_2} C_0 N''_{rs} \rho'_{21} (r_1 s_2) \quad r \geqslant 0, s \leqslant -0.$$

On the right-hand sides of the above equations the positive numerical values of r and s are to be used (whatever their signs on the left-hand side) except when they are suffixed to a or b.

# (b) The Formal Solution of the Equations for $\alpha$ , $\beta$ , $\gamma$ .

If we may solve the linear equations (5.08)-(5.11), each containing an infinite number of unknowns, as if they were finite, we arrive at the results.

$$\begin{cases}
\alpha_{0} - \alpha_{-0} = \frac{\nabla_{0}(a_{mn})}{\nabla(a_{mn})} & \alpha_{r} = \frac{\nabla_{r}(a_{mn})}{\nabla(a_{mn})} & (r = -\infty \text{ to } r = \infty, \text{ excluding } r = 0), \\
\beta'_{0} = -\lambda_{1}\lambda_{2}\frac{\nabla_{0}(b_{mn})}{\nabla(b_{mn})} & \beta_{r} = \frac{\nabla_{r}(b_{mn})}{\nabla(b_{mn})} & (r = -\infty \text{ to } r = \infty, \text{ excluding } r = 0), \\
\gamma_{r} = \frac{\nabla_{r}(c_{mn})}{\nabla(c_{mn})} & (r = -\infty \text{ to } r = +\infty, \text{ including } r = \pm 0).
\end{cases}$$

In these equations  $\nabla (a_{mn})$ ,  $\nabla (b_{mn})$ ,  $\nabla (c_{mn})$  denote the determinants which have  $a_{mn}$ ,  $b_{mn}$ ,  $c_{mn}$  as their general element; in the two latter,  $\pm m$ ,  $\pm n$  range from 0 to  $\infty$ , there being also a central row and a central column in  $\nabla (b_{mn})$  which are not enumerated by m or n. In  $\nabla (a_{mn})$  the values  $\pm 0$  of m and n are not distinct from one another, so that this also has a central column (m=0) and central row (n=0);  $\nabla (c_{mn})$  has not got either of these, since  $\pm 0$  correspond to different rows or columns. The determinant  $\nabla_r$  denotes that obtained from the corresponding  $\nabla$  by replacing all the elements of the  $r^{th}$  column by unity or, in the case only of the central element of the  $r^{th}$  column of  $\nabla_r (b_{mn})$ , by zero. It may be remarked that all these determinants  $\nabla$  and  $\nabla_r$  are infinite in both directions, covering the whole plane. In two quadrants (m, n) both positive or both negative) the determinants  $\nabla$  possess symmetry (cf. (4.23)).

In order to make this investigation complete, from a purely mathematical standpoint, it would clearly be necessary to supplement the above formal solution by a discussion of the questions of convergence raised in the course of our analysis. The complexity of the problem, however, and the rudimentary condition of the theory of infinite determinants, may well absolve the author from an attempt at such a task, for the present. From the standpoint of mathematical physics there is, fortunately, sufficient numerical evidence (cf. § 13e, f, and 'Phil. Trans.,' A, vol. 216, p. 330, Table III.) to afford reasonable assurance that our expressions converge satisfactorily; this is especially so in regard to the formulæ actually used in the applications of f(U, V, W), i.e., (5.22)–(5.25).

# (c) On Certain Combinations of the Coefficients $\alpha$ , $\beta$ , $\gamma$ .

For the purpose of the theory of diffusion, viscosity, and thermal conduction in composite gases, we require only certain combinations of  $\alpha$ ,  $\beta$ ,  $\gamma$ , and never their individual values. The following expressions comprise all those we shall find necessary in this paper; in connection with them we may refer back to (3.13), (3.14), and the formulæ (3.03), (3.04) for f(U, V, W):—

(5.22) 
$$\alpha'_{0} = -\lambda_{1}\lambda_{2}\sum_{0}^{\infty}(\alpha_{r}-\alpha_{-r}),$$

(5.23) 
$$\beta'_{0} = -\lambda_{1}\lambda_{2} \left\{ (\beta_{0} - \beta_{-0}) + \sum_{1}^{\infty} r^{-1} (\beta_{r} - \beta_{-r}) \right\},$$

(5.24) 
$$2h\left(\nu_{1}m_{1}\overline{3U_{1}^{2}-C_{1}^{2}}+\nu_{2}m_{2}\overline{3U_{2}^{2}-C_{2}^{2}}\right)=-\frac{4}{225}C_{0}c_{xx}\sum_{0}^{\infty}\left(\nu_{1}\gamma_{r}+\nu_{2}\gamma_{-r}\right),$$

$$(5^{\circ}25) \quad 2h\left(\nu_{1}m_{1}\overline{\mathsf{U}_{1}}^{2}+\nu_{2}m_{2}\overline{\mathsf{U}_{2}}^{2}\right) = -\frac{2}{9}\mathsf{A}_{0}\xi'_{0}\left\{\frac{5}{2}\left(\nu_{1}\alpha_{0}+\nu_{2}\alpha_{-0}\right)+\sum_{0}^{\infty}\left(r+\frac{5}{2}\right)\left(\nu_{1}\alpha_{r}+\nu_{2}\alpha_{-r}\right)\right\}$$
$$-\frac{2}{9}\mathsf{B}_{0}\frac{\partial\mathsf{T}}{\partial x}\left\{\frac{5}{2}\left(\nu_{1}\beta_{0}+\nu_{2}\beta_{-0}\right)+\sum_{0}^{\infty}\frac{r+\frac{5}{2}}{r}\left(\nu_{1}\beta_{r}+\nu_{2}\beta_{-r}\right)\right\}$$
$$=-\frac{2}{9}\left\{\mathsf{A}_{0}\xi'_{0}\sum_{1}^{\infty}r\left[\left(\nu_{1}\alpha_{r}+\nu_{2}\alpha_{-r}\right)+\mathsf{B}_{0}\frac{\partial\mathsf{T}}{\partial x}\sum_{1}^{\infty}\left(\nu_{1}\beta_{r}+\nu_{2}\beta_{-r}\right)\right\}.$$

We therefore desire to obtain concise expressions for the following quantities:—

(5.26) 
$$\sum_{n=0}^{\infty} (\alpha_r - \alpha_{-r}), \qquad \beta_0 - \beta_{-0} + \sum_{n=1}^{\infty} r^{-1} (\beta_r - \beta_{-r}),$$

(5.27) 
$$\sum_{1}^{\infty} r \left( \nu_{1} \alpha_{r} + \nu_{2} \alpha_{-r} \right), \qquad \sum_{1}^{\infty} \left( \nu_{1} \beta_{r} + \nu_{2} \beta_{-r} \right), \qquad \sum_{0}^{\infty} \left( \nu_{1} \gamma_{r} + \nu_{2} \gamma_{-r} \right).$$

The denominators in the expressions (5.21) for  $\alpha_r$ ,  $\beta_r$ ,  $\gamma_r$  are independent of r. Hence our problem consists in the combination of the numerator determinants  $\nabla_r$  for an infinite number of values of r.

# (d) Difference-Transformations of Infinite Determinants.

It is convenient at this stage to describe certain operations, by the application of which we are enabled to preserve the symmetry and increase the convenience of our determinantal formulæ. These operations will be termed "continued differencing" by rows, by columns, or by rows and columns, and we shall denote the corresponding symbolic operators by  $\delta_{0s}$ ,  $\delta_{r0}$ , or  $\delta_{rs}$  respectively. We shall first define them in relation to infinite determinants which cover only a quadrant of the infinite plane  $(r \geqslant 0, s \geqslant 0)$ , and afterwards in relation to the more complicated type which occurs in this paper.

The operation of continued differencing by rows  $(\delta_{0s})$  or by columns  $(\delta_{r0})$ , applied to the determinant  $\nabla (f_{rs})$ , where  $r \geqslant 0$ ,  $s \geqslant 0$ , transforms it into the determinant  $\nabla (\delta_{0s}f_{rs})$  or  $\nabla (\delta_{r0}f_{rs})$  respectively, where

(5.28) 
$$\delta_{0s} f_{rs} \equiv \sum_{n=0}^{s} (-1)^{n} {}_{s} C_{n} f_{r,s-n}, \qquad \delta_{r0} f_{rs} \equiv \sum_{m=0}^{r} (-1)^{m} {}_{r} C_{m} f_{r-m.s}.$$

We may effect the operation  $\delta_{0s}$  as follows: from each element of row s we subtract the corresponding element of row s-1, for every row from s=1 onwards: this done, we repeat the operation on the transformed determinant, except that we now begin at s=2: and this process is continued without end, beginning each time with the row next after the initial row on the previous occasion. It may readily be seen that the result is as we have already stated, and that the value of the determinant is unaffected by the operation. Continued differencing by columns is strictly analogous, and need not be separately described. Continued differencing by rows and columns is performed by applying the two separate operations successively, the order being immaterial. Without alteration in value, the determinant is thus changed in form from  $\nabla (f_{rs})$  to  $\nabla (\delta_{rs} f_{rs})$ , where (cf. (5.28))

(5.29) 
$$\delta_{rs}f_{rs} = \delta_{r0}\left(\delta_{0s}f_{rs}\right) = \delta_{0s}\left(\delta_{r0}f_{rs}\right) = \sum_{m=0}^{n} \sum_{n=0}^{s} (-1)^{m+n} {}_{r}C_{m,s}C_{n}f_{r-m,s-n}.$$

In the case of determinants which are infinite in both directions, the operation of continued differencing by rows and columns is effected by applying the process described above to each separate quadrant; thus the differencing by rows is performed by differencing outwards from the centre row in both directions (above and below), and likewise, by columns, both to right and left of the centre column. Neither of these partial operations, nor the complete process, alters the value of the determinant, a fact which we may express by the equation

(5.30) 
$$\nabla (f_{rs}) = \nabla (\delta_{r0} f_{rs}) = \nabla (\delta_{0s} f_{rs}) = \nabla (\delta_{rs} f_{rs}),$$

where the notation is similar to that used in the former case. There, however, r, s, and consequently also m, n, were necessarily positive or zero, while our convenient notation for determinants of the present type involves also negative values of r and s.

In order to make the former definitions of  $\delta_{r0}$ ,  $\delta_{0s}$ ,  $\delta_{rs}$  applicable to this case, we must adopt certain conventions as to the interpretation of  $(5^{\circ}28)$ ,  $(5^{\circ}29)$ , to allow for negative quantities. These conventions are (a) that in  ${}_{r}C_{m,s}C_{n}$  the positive numerical values of r and s, m and  $n^*$  are to be used in all cases: and (b) that r-m and s-n retain the same signs as r and s respectively even when m=r, n=s. The latter rule preserves, in relation to  $f_{rs}$ , the distinction between +0 and -0 which in certain cases we desire to maintain.

(e) A Symmetrical Expression for 
$$\sum_{n=0}^{\infty} (\alpha_r - \alpha_{-r})$$
.

In discussing  $\Sigma(\alpha_r - \alpha_{-r})$  it is convenient to change our notation for  $\nabla_r(\alpha_{mn})$ , writing it in the form  $\nabla(r_r\alpha_{mn})$  to denote the determinant whose  $(m, n)^{\text{th}}$  element is  $r_r\alpha_{mn}$ . If we define  $r_r\alpha_{mn}$  by the equations

(5.31) 
$$_{r}a_{mn} \equiv a_{mn} \quad (m \neq r), \quad _{r}a_{rn} = 1, \quad _{r}a_{m0} \equiv _{r}a_{m,-0}$$

we make  $\nabla (ra_{mn})$  identical with  $\nabla_r (a_{mn})$  as defined in § 5 (b), and therefore, by (5.21),

(5.32) 
$$\alpha_0 - \alpha_{-0} = \frac{\nabla \left( \alpha_{mn} \right)}{\nabla \left( \alpha_{mn} \right)}, \qquad \alpha_r = \frac{\nabla \left( \alpha_{mn} \right)}{\nabla \left( \alpha_{mn} \right)}, \quad (r \neq 0).$$

By applying the operation of continued differencing by rows to  $\nabla (ra_{mn})$  we transform it into  $\nabla (\delta_{0n.r}a_{mn})$ , where  $\delta_{0n.r}a_{mn}$  is defined by (5.28) (putting  $f_{mn} = ra_{mn}$ , and making no distinction between  $f_{m0}$  and  $f_{m,-0}$ —cf. the third equation of (5.31)). Now it is readily evident that

(5.33) 
$$\delta_{0n.r}a_{mn} = \delta_{0n}a_{mn} \quad (m \neq r), \qquad \delta_{0n.r}a_{rn} = 0 \quad (n \neq 0), \qquad \delta_{00.r}a_{r0} = 1,$$

so that  $\nabla (\delta_{0n}, a_{mn})$ , and consequently, also,  $\nabla_r (a_{mn})$ , is equal to  $\nabla'_r (\delta_{0n}, a_{mn})$ , this being defined as identical with  $\nabla (\delta_{0n}, a_{mn})$  except that in the  $r^{\text{th}}$  column the central element is unity, while all the others are zero. Hence  $\nabla'_r (\delta_{0n} a_{mn})$  is clearly equal to the minor of the  $r^{\text{th}}$  element of the central row in  $\nabla (\delta_{0n} a_{mn})$ . If we replace the elements of this central row by  $+1 \ (m \geqslant 0)$  or  $-1 \ (m < 0)$ , and denote the result by  $\nabla' (\delta_{0n} a_{mn})$ , we may evidently write (cf. (5.32))

$$\sum_{0}^{\infty} (\alpha_{r} - \alpha_{-r}) = \frac{\nabla' (\delta_{0n} \alpha_{mn})}{\nabla (\alpha_{mn})} = \frac{\nabla' (\delta_{0n} \alpha_{mn})}{\nabla (\delta_{0n} \alpha_{mn})}$$

by (5.30).

We next apply to  $\nabla (\delta_{0n}a_{mn})$  and  $\nabla'(\delta_{0n}a_{mn})$  the operation of continued differencing by columns, so as to transform them into  $\nabla (\delta_{mn}a_{mn})$  and  $\nabla'(\delta_{mn}a_{mn})$ . We make one slight difference of rule here, as compared with the former differencing by rows: that is, in (5.29) we shall preserve the distinction between m=0 and m=-0, writing  $f_{0n}$ 

<sup>\*</sup> The signs of m, n are the same, of course, as those of r, s respectively.

for the elements of the central column in  $\nabla$  or  $\nabla'$ , and defining  $f_{-0n}$  as equal to  $-f_{0n}$ . This means, in effect, that the elements of the central column are to be reversed in sign, for the purpose of differencing on the left (in < 0).\* Now, by definition,  $\nabla'(\delta_{0n}a_{mn})$  differs from  $\nabla(\delta_{0n}a_{mn})$  only in the central row, for which

$$f_{m0} = 1 \quad (m \geqslant 0), \qquad f_{m0} = -1 \quad (m < 0), \quad \text{and also} \quad f_{-00} \equiv -1,$$
 so that

$$\delta_{m0} f_{m0} = 0$$
 if  $m \neq 0$ ,  $\delta_{00} f_{00} = 1$ .

Hence, when transformed into  $\nabla'(\delta_{mn}a_{mn})$ , it differs from  $\nabla(\delta_{mn}a_{mn})$  only in the central row, all the elements of which are zero except the central one, which is unity. In other words,  $\nabla'(\delta_{mn}a_{mn})$  is the principal minor of  $\nabla(\delta_{mn}a_{mn})$ , and the expression for  $\sum_{n=0}^{\infty} (\alpha_r - \alpha_{-r})$ , viz.,

$$\sum_{0}^{\infty} (\alpha_{r} - \alpha_{-r}) = \frac{\nabla' (\delta_{mn} \alpha_{mn})}{\nabla (\delta_{mn} \alpha_{mn})} = -\frac{\alpha'_{0}}{\lambda_{1} \lambda_{2}}$$

has thus been reduced to a concise symmetrical form.

(f) A Symmetrical Expression for  $\beta'_0$ .

It appears from (5.21) that

$${eta'_{\scriptscriptstyle 0}} = -\lambda_{\scriptscriptstyle 1}\lambda_{\scriptscriptstyle 2} rac{
abla_{\scriptscriptstyle 0}\left(b_{\scriptscriptstyle mn}
ight)}{
abla\left(b_{\scriptscriptstyle mn}
ight)},$$

where  $\nabla_0$  is the same as  $\nabla$ , except that all the elements of the central column are unity save the central one, which is zero. If we transform  $\nabla$  and  $\nabla_0$  by the operations described in § 5 (d), differencing by columns with m = 1 (for the right) and m = -1 (for the left) as starting points, and similarly for the rows, we leave the central column (not enumerated by m) untouched as regards the first part of the operation, and the central row untouched by the second part. Thus we obtain the result

$$\beta'_{0} = -\lambda_{1}\lambda_{2} \frac{\nabla'_{0} \left(\delta_{mn}b_{mn}\right)}{\nabla \left(\delta_{mn}b_{mn}\right)},$$

where  $\nabla (\delta_{mn}b_{mn})$  is the determinant whose general element is  $\delta_{mn}b_{mn}(\pm m, \pm n \text{ ranging})$  from 0 to  $\infty$ ), and which has a central column  $\delta_{0n}b_n$ , a central row  $\delta_{m0}b_m$ , and b as the central element. From this determinant we obtain  $\nabla'_0(\delta_{mn}b_{mn})$  by substituting zero for all the elements of the central column except those next to the centre on either side  $(n = \pm 0)$  which are replaced by unity.

<sup>\*</sup> We may note that the elements of the central column are the coefficients of  $\alpha_0$  in (5.01)-(5.05), while the elements reversed in sign are the coefficients of  $\alpha_{-0}$ .

(g) Symmetrical Expressions for 
$$\sum_{1}^{\infty} r(\nu_1 \alpha_r + \nu_2 \alpha_{-r})$$
,  $\sum_{1}^{\infty} (\nu_1 \beta_r + \nu_2 \beta_{-r})$ ,  $\sum_{0}^{\infty} (\nu_1 \gamma_r + \nu_2 \gamma_{-r})$ .

As in  $\S 5$  (e) we may prove that

$$\sum_{1}^{\infty} r\left(\nu_{1} \alpha_{r} + \nu_{2} \alpha_{-r}\right) = \frac{\nabla_{0}\left(\delta_{0n} \alpha_{mn}\right)}{\nabla\left(\delta_{0n} \alpha_{mn}\right)},$$

where  $\nabla_0 (\delta_{0n} a_{mn})$  is identical with  $\nabla (\delta_{0n} a_{mn})$  except in the central row, the elements of which are equal to  $r_{\nu_1}(r \geqslant 0)$  or  $r_{\nu_2}(r \leqslant 0)$ , the positive numerical value of r being taken in both cases. On applying the operation of continued differencing by columns we obtain the result

(5.37) 
$$\sum_{1}^{\infty} r\left(\nu_{1}\alpha_{r} + \nu_{2}\alpha_{-r}\right) = \frac{\nabla_{0}\left(\delta_{mn}\alpha_{mn}\right)}{\nabla\left(\delta_{mn}\alpha_{mn}\right)},$$

where  $\nabla_0 (\delta_{mn} a_{mn})$  differs from  $\nabla (\delta_{mn} a_{mn})$  only in the central row, all the elements of which are zero save those on either side the centre (r = 1 and r = -1), which are respectively equal to  $\nu_1$  and  $\nu_2$ . This follows from the fact that

$$\delta_{r_0} r = 0 \quad (r \neq 1), \qquad \delta_{r_0} r = 1 \quad (r = 1).$$

Again, from (5.21), we may prove in the usual way that

$$\beta_r = \frac{\nabla_r \left( \delta_{0n} b_{mn} \right)}{\nabla \left( \delta_{0n} b_{mn} \right)},$$

where  $\nabla_r$  and  $\nabla$  are the same, except that in the  $r^{\text{th}}$  column of  $\nabla_r$  all the elements are zero save those on either side the centre (i.e.,  $n = \pm 0$ ) which are unity. If in  $\nabla$  and  $\nabla_r$  we add half of each of the rows  $n = \pm 0$  to the centre row, and subtract this new centre row from the rows  $n = \pm 0$ ,  $\nabla$  becomes transformed into  $\nabla (\delta_{0n}b'_{mn})$ , where  $b'_{mn} = b_{mn}$ , except when  $n = \pm 0$ , while

$$(5.38) \quad b'_{m0} = \frac{1}{2} (b_{m0} - b_{m-0}) - b_m, \quad b'_{m-0} = \frac{1}{2} (b_{m-0} - b_{m0}) - b_m, \quad b'_m = b_m + \frac{1}{2} (b_{m0} + b_{m-0}).$$

Similarly,  $\nabla_{\tau}$  becomes transformed into  $\nabla_{\tau}(\delta_{0n}b'_{mn})$ , identical with  $\nabla(\delta_{0n}b'_{mn})$ , except that in the  $r^{\text{th}}$  column all the elements are zero save the central one, which is unity.

Consequently we may write

$$\sum_{1}^{\infty} \left( \nu_{1} \beta_{r} + \nu_{2} \beta_{-r} \right) = \frac{\nabla_{0} \left( \delta_{0n} b'_{mn} \right)}{\nabla \left( \delta_{0n} b'_{mn} \right)},$$

where  $\nabla_0$  is the same as  $\nabla$  except that in the central row all the elements on the right of the centre  $(m \ge 0)$  are equal to  $\nu_1$ , all those to the left  $(m \le -0)$  are equal to  $\nu_2$ , while the central element is zero. We now "difference" by columns, with the result

$$\sum_{1}^{\infty} \left(\nu_{1} \beta_{r} + \nu_{2} \beta_{-r}\right) = \frac{\nabla_{0} \left(\delta_{mn} b'_{mn}\right)}{\nabla \left(\delta_{mn} b'_{mn}\right)}.$$

The general element of  $\nabla$  is  $\delta_{mn}b_{mn}$  or  $\delta_{mn}b'_{mn}$ , which are the same except when  $n=\pm 0$ ; the general elements of these two rows are  $\delta_{m0}b'_{m0}$ ,  $\delta_{m-0}b'_{m-0}$  (cf. (5.38)), the general elements of the central row and column respectively are  $\delta_{m0}b'_{m}$  and  $\delta_{0n}b_{n}$ , while the central element is b. From this we obtain  $\nabla_{0}$  if we replace all the elements of the central row by zero, except the two on either side the centre, which are  $\nu_{1}$  (m=0) and  $\nu_{2}$  (m=-0).

Finally, we may prove that

(5.40) 
$$\sum_{0}^{\infty} \left( \nu_{1} \gamma_{r} + \nu_{2} \gamma_{-r} \right) = \frac{\nabla_{0} \left( \delta_{mn} c_{mn} \right)}{\nabla \left( \delta_{mn} c_{mn} \right)},$$

where  $\nabla$  is defined as usual  $(\pm m, \pm n \text{ ranging from } 0 \text{ to } \infty)$ , while in  $\nabla_0$  all the elements are equal to the corresponding elements of  $\nabla$  except in the two central rows  $(n = \pm 0)$ . In the row n = 0 all the elements are zero except the central two, which are  $\nu_1(m = 0)$  and  $\nu_2(m = -0)$ . In the row n = -0 the general element is  $c_{m-0}-c_{m0}$ .

## § 6. The Complete Solution for Maxwellian Molecules.

In the case of Maxwellian molecules, *i.e.*, molecules which are point centres of force varying inversely as the fifth power of the distance, the solution reduces to finite terms. This arises from the fact (cf. § 9 (C), 'Phil. Trans.,' A, vol. 216, p. 323) that for such a law of inter-action the functions  $\phi$ ,  $\psi$ ,  $\chi$  are independent of y, with the result that for all values of t we have (cf. (4.25))

(6.01) 
$$k_t = 1, \qquad k_{11}^t = k_{11}^0, \qquad k_{12}^t = k_{12}^0, \qquad k_{22}^t = k_{22}^0,$$

and consequently,

(6.02) 
$$\sum_{t=0}^{s} {}_{s}C_{t}\mu_{1}^{s-t}\mu_{2}^{t}k_{t} = \sum_{t=0}^{s} {}_{s}C_{t}\mu_{1}^{s-t}\mu_{2}^{t} = (\mu_{1} + \mu_{2})^{s} = 1.$$

From (5.12)-(5.14) and (4.27), (4.29), with the aid of (6.02), we deduce that

(6.03) 
$$a_{00} = a_{0s} = a_{r0} = \frac{2}{2.7} \frac{m_1 m_2}{m_1 + m_2} \lambda_1 \lambda_2 \nu_0 \Lambda_0 K'_{12}(0),$$

independently of the value of r or s. From (5.21) and (3.13) we consequently have

(6.04) 
$$\alpha_r = 0 \quad (r \neq 0), \quad \alpha_0 - \alpha_{-0} = \frac{1}{\alpha_{00}} = -\frac{\alpha'_0}{\lambda_1 \lambda_2}, \quad \alpha_0 = -\frac{\alpha'_0}{\lambda_1}, \quad \alpha_{-0} = \frac{\alpha'_0}{\lambda_2}.$$

Again, from (6.03) and (5.16), (5.17) we conclude that  $b_r = 0 = b_s$  for all values of  $\pm v$ ,  $\pm s$  from 0 to  $\infty$ . Hence, by (5.36), or more simply from (5.21)—since in  $\nabla_0(b_{mn})$  all the elements of the central column are zero, instead of all except one, the central element, as in  $\nabla$ —we have

$$\beta'_0 = 0.$$

Also in  $\nabla(b_{mn})$  and  $\nabla_r(b_{mn})$  we may in this case omit the central row and column, all the elements of which are zero (if  $r \neq 0$ ) except the central element, which is the same in each (b); we suppose that this is done, so that  $\nabla$  and  $\nabla_r$  become determinants which possess no single central row or column, just as with  $\nabla(c_{mn})$ . We will consider the two central columns of  $\nabla(b_{mn})$  and  $\nabla(c_{mn})$  corresponding to  $m = \pm 0$ . We have, by (5.12)–(5.18), (4.35)–(4.38), and (6.03),

(6.06) 
$$s > 0$$
,  $b_{0s} = \frac{1}{\lambda_1} \frac{B_0}{A_0 R} \frac{1}{s+1} (a_{1,s+1} - a_{0,s+1})^{-1}$   

$$= \frac{64\pi m_1}{675 R} B_0 K'_{12}(0) \{ \nu_1 + 5\mu_2 \nu_2 (3\mu_1^2 + \mu_2^2 + \frac{4}{5}\mu_1 \mu_2 k_{12}^{-0}) \},$$

(6.07) 
$$s < 0$$
,  $b_{-0s} = -\frac{64\pi m_2}{675 \,\mathrm{R}} B_0 K'_{12}(0) \{ \nu_2 + 5\mu_1 \nu_1 (3\mu_2^2 + \mu_1^2 + \frac{4}{5}\mu_1 \mu_2 k_{12}^0) \},$ 

(6.08) 
$$s > 0$$
,  $b_{-\theta s} = -\frac{16\pi m_2}{135 R} B_0 K'_{12}(0) \mu_1 \mu_2^2 (1 + \frac{1}{5} k_{12}^0)$ ,

(6.09) 
$$s < 0$$
,  $b_{0s} = \frac{16\pi m_1}{135 \text{R}} B_0 K'_{12}(0) \mu_1^2 \mu_2 (1 + \frac{1}{5} k^0_{12})$ ,

(6.10) 
$$s > 0$$
,  $c_{0s} = \frac{32}{15^3} \pi C_0 K'_{12}(0) [3\nu_1 k_{11}^0 + 2\mu_2 \nu_2 (10\mu_1 + 3\mu_2 k_{12}^0)],$ 

(6.11) 
$$s > 0$$
,  $c_{-0s} = \frac{32}{15^3} 2\pi \mu_2 \nu_2 C_0 K'_{12}(0) (-10\mu_1 + 3\mu_1 k_{12}^0)$ ,

(6.12) 
$$s < 0$$
,  $c_{0s} = \frac{32}{15^3} 2\pi \mu_1 \nu_1 C_0 K'_{12}(0) (-10\mu_2 + 3\mu_2 k_{12}^0)$ ,

(6.13) 
$$s < 0$$
,  $c_{-0s} = \frac{32}{15^3} \pi C_0 K'_{12}(0) \left[ 3\nu_2 k_{22}^0 + 2\mu_1 \nu_1 \left( 10\mu_2 + 3\mu_1 k_{12}^0 \right) \right].$ 

All these quantities, it will be noticed, are independent of s; thus we see that in  $\nabla(b_{mn})$  and  $\nabla(c_{mn})$  the elements of the two centre columns take only four distinct values, all the elements of these columns which are in the same quadrant having the same value.

By using the method of differencing by rows it is easy to prove, as a consequence of the property of  $\nabla(b_{mn})$  and  $\nabla(c_{mn})$  which we have just established, that

(6.14) 
$$\beta_r = 0 \quad (r \geqslant 2, \ r \leqslant -2), \qquad \gamma_r = 0 \quad (r \geqslant 1, \ r \leqslant -1),$$

while (cf. (6.05), (6.14), (3.14)),

(6.15) 
$$\gamma_0 = \frac{c_{-00} - c_{-0-0}}{c_{-00} c_{0-0} - c_{00} c_{-0-0}}, \qquad \gamma_{-0} = \frac{c_{00} - c_{0-0}}{c_{00} c_{-0-0} - c_{0-0} c_{-00}},$$

(6.16) 
$$\beta_0 = -\beta_1 = \frac{b_{-0-0} - b_{-00}}{b_{-00} b_{-0-0} - b_{00} b_{-0-0}}, \qquad \beta_{-0} = -\beta_{-1} = \frac{|b_{00} - b_{0-0}|}{b_{0-0} b_{-\infty} - b_{00} b_{-0-0}}$$

Consequently, in the case of Maxwellian molecules,  $F(c^2)$  and  $H(c^2)$  each reduce to their first terms, while  $G(c^2)$  reduces to two terms only, the solution being quite finite.

#### § 7. The General Solution when $m_1:m_2$ is Very Large.

When the mass  $m_1$  of the heavier molecules is very large compared with that of the lighter molecules, so that  $m_2/m_1$  may be supposed zero, an exact general solution may be obtained in simple terms. This was first proved by LORENTZ,\* in connection with the theory of electrons. His method is much simpler than that of this paper, from which, however, his results may, with little difficulty, be deduced as a very special case. The deduction will be described in some detail, since the knowledge of the exact solution throws valuable light on the convergence of our successive approximations; it also leads to an expression for  $\pi$  which is of interest, as being in a form which, so far as my knowledge goes, is new.

We suppose that the effect of collisions between the molecules  $m_2$  is negligible, so that  $\rho_{22}$  and  $\rho'_{22}$  may be omitted from our calculations; if the molecules are rigid elastic spheres of radii  $\sigma_1:\sigma_2$ , this amounts to the neglect of  $\sigma_2^2/\sigma_1^2$  (cf. § 9 (f)) or, in general, to  $\phi_{22}/\phi_{11}$ .

It may readily be seen from (4.13), (4.14) that if  $m_2 = 0$  the value of  $B^k(m, n)$ , with whatever suffix, is zero except when k = 0, and that

(7.01) 
$$\begin{cases} B_{1212}^{0}(m,n) = (2x^{2})^{m+n}, & B_{2112}^{0}(m,n) = 2^{m+n}y^{2m}x^{2n}, \\ B_{2121}^{0}(m,n) = (2y^{2})^{m+n}, & B_{1221}^{0}(m,n) = 2^{m+n}x^{2m}y^{2n}. \end{cases}$$

We also require  $B^1(m, n)$  to the first order in  $m_2$ , as follows:—

(7.02) 
$$\begin{cases} B_{1212}^{1}(m,n) = \frac{4}{9}mn\mu_{2}2^{m+n}x^{2(m+n-1)}y^{2}, & B_{2112}^{1}(m,n) = \frac{4}{9}mn\mu_{2}2^{m+n}y^{2m}x^{2n}, \\ B_{2121}^{1}(m,n) = \frac{4}{9}mn\mu_{2}2^{m+n}y^{2(m+n-1)}x^{2}, & B_{1221}^{1}(m,n) = \frac{4}{9}mn\mu_{2}2^{m+n}x^{2m}y^{2n}. \end{cases}$$

From these, by means of (4.07)–(4.12) we deduce the following expressions for  $\rho(r, s)$ ,  $\rho'(r, s)$ , retaining only the terms of highest order:—

$$(7.03) \qquad \rho_{12}(r_1s_1) = \frac{4}{9}\pi\nu_1\nu_2\mu_2 2^{r+s} \left(2rs + r + s + \frac{3}{2}\right) \left(r + s + \frac{1}{2}\right)_{r+s} \mathbb{K}'_{12}(0),$$

$$(7.04) \qquad \rho_{12}(r_2 s_1) = -\frac{4}{9} \pi \nu_1 \nu_2 \mu_1 2^{r+s} (r + \frac{3}{2})_{r+1} (s + \frac{3}{2})_s k_r \mathbf{K}'_{12}(0),$$

$$(7.05) \qquad \rho_{21}(r_1s_2) = -\frac{4}{9}\pi\nu_1\nu_2\mu_2 2^{r+s} (r+\frac{3}{2})_{r+1} (s+\frac{3}{2})_s k_s K'_{12}(0),$$

\* LORENTZ, 'Archives Néerlandaises,' 10, p. 336, 1905; 'Theory of Electrons,' p. 268. A more general form of Lorentz's theory is given in Jeans' 'Dynamical Theory of Gases,' 2nd ed., §§ 314, et seq. I am indebted to Mr. Jeans for pointing out the interest of a detailed comparison of Lorentz's theory with this special case of my own, and in consequence I have rewritten § 7 with greater fullness than at first.

$$(7.06) \qquad \rho_{21}(r_2s_2) = \frac{4}{9}\pi\nu_1\nu_2\mu_1 2^{r+s} (r+s+\frac{3}{2})_{r+s+1} k_{r+s} K'_{12}(0),$$

$$(7.07) \qquad \rho'_{12}(r_1s_1) = \frac{3}{4} \frac{2}{5} \pi \nu_1 \nu_2 \mu_2 2^{r+s} \left( rs + r + s + \frac{5}{2} \right) \left( r + s + \frac{3}{2} \right)_{r+s+1} \mathcal{K}'_{12}(0),$$

$$\begin{cases} \rho'_{12}(r_{2}s_{1}) = \frac{8}{45}\pi\nu_{1}\nu_{2}\mu_{1}2^{r+s}rs(r+\frac{5}{2})_{r+2}(s+\frac{1}{2})_{s}k_{r+1}K'_{12}(0), & r > 0, s > 0. \\ \rho'_{12}(0_{2}s_{1}) = \frac{3}{45}\pi\nu_{1}\nu_{2}\mu_{2}2^{s}(s+\frac{5}{2})_{s+2}(-k_{0}+\frac{3}{10}k_{12}^{0})K'_{12}(0) = \rho'_{21}(s_{1}0_{2}), \\ \rho'_{12}(r_{2}0_{1}) = \frac{3}{45}\pi\nu_{1}\nu_{2}\mu_{2}2^{r}(r+\frac{5}{2})_{r+2}(-k_{r}+\frac{3}{10}k^{r}_{12})K'_{12}(0) = \rho'_{21}(0_{1}r_{2}), \end{cases}$$

$$(7.09) \qquad \rho'_{21}(r_1s_2) = \frac{8}{45}\pi\nu_1\nu_2\mu_1 2^{r+s} rs \left(r + \frac{1}{2}\right)_r \left(s + \frac{5}{2}\right)_{r+2} k_{s+1} K'_{12}(0), \qquad r > 0, s > 0,$$

$$(7.10) \qquad \rho'_{21}(r_2s_2) = \frac{16}{75}\pi\nu_1\nu_2\mu_1 2^{r+s} \left(r+s+\frac{5}{2}\right)_{r+s+2} k_{12}^{r+s+1} K'_{12}(0).$$

For the particular values of r and s there dealt with, the expressions (4.26)-(4.34) reduce to the above in the present special case, as may readily be verified.

We now substitute from (7.03)–(7.10) in (5.12)–(5.20), retaining only the terms of the highest order; and neglecting quantities of order  $m_2^2: m_1^2$ ; the result is as follows:—

(7.11) 
$$s \geqslant 0$$
,  $\alpha_{0s} = \frac{2}{27}\pi\lambda_1\lambda_2\nu_0 m_1\mu_2 A_0 K'_{12}(0) = \alpha_{00}$ ,  $s \leqslant 0$ ,  $\alpha_{0s} = \frac{2}{27}\pi\lambda_1\lambda_2\nu_0 m_1\mu_2 A_0 k_s K'_{12}(0)$ ,

(7.12) 
$$r > 0, s \gg 0, \qquad a_{rs} = \frac{m_1}{\nu_0} N_{rs} \rho_{11} (r_1 s_1),$$

(7.13) 
$$r < 0, s \le 0, \qquad \alpha_{rs} = -\frac{2}{2.7}\pi\lambda_1\lambda_2\nu_0 m_2\mu_1 A_0 \frac{(r+s+\frac{3}{2})_{r+s}}{(r+\frac{3}{2})_r(s+\frac{3}{2})_s} k_{r+s} K'_{12}(0),$$

(7.14) 
$$(r < 0, s > 0), \qquad \alpha_{rs} = -\frac{2}{27}\pi\lambda_1\lambda_2\nu_0 m_2\mu_1 A_0 k_r K'_{12}(0),$$

(7.15) 
$$(r > 0, s < 0), \qquad \alpha_{rs} = \frac{2}{27} \pi \lambda_1 \lambda_2 \nu_0 m_1 \mu_2 A_0 k_s K'_{12}(0),$$

(7.16) 
$$(r \geqslant 0)$$
,  $b_r = 0$ ,  $b = \frac{B_0}{A_0 R} a_{00}$ ,  $b_r = -\frac{2}{277} \frac{\pi}{R} \lambda_1 \lambda_2 \nu_0 m_1 \mu_2 B_0 \frac{k_{r+1} - 1}{r+1} K'_{12}(0)$ ,  $(r \leqslant -0)$ .

(7°17) 
$$(s \geqslant 0)$$
,  $b_s = 0$ ;  $b_s = -\frac{1}{\lambda_2} \frac{2}{27} \frac{\pi}{R} \lambda_1 \lambda_2 \nu_0 m_1 \mu_2 B_0 \frac{k_{s+1} - 1}{s+1} K'_{12}(0)$ ,  $(s \leqslant -0)$ ,

$$(7.18) (r \leqslant -0, s \geqslant 0), b_{rs} = 0, (r \geqslant 0, s \leqslant -0),$$

(7.19) 
$$(r \geqslant 0, s \geqslant 0),$$
  $b_{rs} = \frac{1}{\lambda_1} \frac{2}{27} \frac{\pi}{R} \lambda_1 \lambda_2 \nu_0 m_2 \mu_1 B_0 \frac{1}{(r+1)(s+1)}$ 

$$\left\{ \frac{(r+s+\frac{7}{2})_{r+s}}{(r+\frac{5}{2})_r (s+\frac{5}{2})_s} k_{r+s+2} - k_{r+1} - k_{s+1} + 1 \right\} K'_{12}(0).$$

Since, by (7.14), (7.15),  $\alpha_{rs}$   $(r < 0, s \ge 0)$  is independent of s, and  $\alpha_{rs}$   $(r > 0, s \le 0)$  is independent of r, it is readily evident that in the alternate quadrants of the determinants  $\nabla (\delta_{mn}\alpha_{mn})$  and  $\nabla' (\delta_{mn}\alpha_{mn})$  all the elements vanish. Hence each  $\nabla$  becomes

equal to the product of the two remaining quadrants; in the positive quadrant the determinants are the same (r > 0, s > 0). Consequently in this case (5.35) becomes

(7.20) 
$$\alpha'_{0} = -\lambda_{1}\lambda_{2}\sum_{0}^{\infty} (\alpha_{r} - \alpha_{-r}) = -\frac{27}{2\pi\nu_{0}m_{2}A_{0}K'_{12}(0)}\frac{D_{0}}{D}$$

where D is the determinant whose general element is

(7.21) 
$$\delta_{rs}\alpha_{rs} = \delta_{rs} \frac{(r+s+\frac{3}{2})_{r+s}}{(r+\frac{3}{2})_{r}(s+\frac{3}{2})_{s}} k_{r+s}, \qquad r \geqslant 0, \ s \geqslant 0,$$

and D<sub>0</sub> is its principal minor.

Similarly, it follows from (5.36) and (7.16)–(7.19) that  $\beta'_0$  can be likewise expressed as the quotient by an infinite determinant (covering only a quadrant of the infinite plane) of its *second* minor, as follows:—

(7.22) 
$$\beta'_{0} = -\frac{27 R \lambda_{2}}{2 \pi \nu_{0} m_{2} B_{0} K'_{12}(0)} \frac{D'_{1}}{D'}.$$

Here D' is the determinant whose general element  $d_{rs}$  is given by

$$(7.23) (r > 0, s > 0) d_{rs} = \delta_{r-1, s-1} \frac{1}{rs} \left\{ \frac{(r+s+\frac{3}{2})_{r+s}}{(r+\frac{3}{2})_r (s+\frac{3}{2})_s} k_{r+s} - k_r - k_s + 1 \right\}$$

$$= \frac{1}{rs} \delta_{rs} \frac{(r+s+\frac{3}{2})_{r+s}}{(r+\frac{3}{2})_r (s+\frac{3}{2})_s} k_{r+s},$$

$$(7.24) r > 0 d_{r0} = d_{0r} = \delta_{r-1} \frac{1}{r} (k_r - 1) = \frac{1}{r} \delta_r k_r d_{00} = 1.$$

Thus it is the same as the determinant D of (7.20) except that the  $r^{\text{th}}$  row and column  $(r \ge 1)$  are divided throughout by r. The determinant D'<sub>1</sub> is the second minor of D', *i.e.*, the minor of the next element to the centre in the first row or column.

Again, from (5.37), we may prove that

(7.25) 
$$\sum_{1}^{\infty} r(\nu_{1}\alpha_{r} + \nu_{2}\alpha_{-r}) = -\frac{27\nu_{0}}{2\pi\nu_{1}m_{2}A_{0}K'_{12}(0)} \frac{D_{1}}{D},$$

where D<sub>1</sub> is the second minor of D just as D'<sub>1</sub> is of D'. It is easy to see that\*

$$\frac{D_1}{D} = \frac{D'_1}{D'}.$$

Likewise, from (5.39), we have

(7.27) 
$$\sum_{1}^{\infty} (\nu_{1}\beta_{r} + \nu_{2}\beta_{-r}) = -\frac{27\nu_{0}}{2\pi\nu_{1}m_{2}B_{0}K'_{12}(0)} \frac{D''_{1}}{D''},$$

\* *Cf.* the footnote on p. 154, indicating that  $\sum r(\nu_1 \alpha_r + \nu_2 \alpha_{-r})$  is, quite generally, a mere multiple of  $\beta'_0$ .

where D" is the determinant which is identical with D' except in its first two rows (for which cf. (5.38)), while D"<sub>1</sub> is the minor of the second element in the first row of D".

#### § 8. THE GENERAL SOLUTION FOR THE CASE OF SIMILAR MOLECULES.

Another instructive and specially simple particular case is that of a gas composed of two sets of molecules whose mechanical properties—mass and mode of inter-action during encounter—are identical. In this case all the symbols which we have distinguished by the suffixes 1 or 2, to indicate reference to one or other molecular group, now have the same value for either suffix, with the exception of  $\nu_1$ ,  $\nu_2$  or  $\lambda_1$ ,  $\lambda_2$ , which denote the numbers or proportions of the two molecular groups. Moreover  $(cf. (4.01)-(4.04), (4.07)-(4.12), \text{ or, for a simpler and more general explanation, 'Phil. Trans.,' A, vol. 216, § 7 (H), p. 309), we have$ 

(8.01) 
$$\frac{1}{\nu_1^2} \rho_{11}(r_1 s_1) = \frac{1}{\nu_2^2} \rho_{22}(r_2 s_2) = \frac{1}{\nu_0^2} \rho(r, s),$$

$$(8.02) \ \rho_{12}(r_1s_1) + \rho_{12}(r_2s_1) = \rho_{21}(r_2s_2) + \rho_{21}(r_1s_2) = \lambda_1\lambda_2\rho(r,s) \qquad \rho_{12}(r_2s_1) = \rho_{21}(r_1s_2),$$

(8.03) 
$$\frac{1}{\nu_1^2} \rho'_{11}(r_1 s_1) = \frac{1}{\nu_2^2} \rho'_{22}(r_2 s_2) = \frac{1}{\nu_0^2} \rho'(r, s),$$

(8.04) 
$$\rho'_{12}(r_1s_1) + \rho'_{12}(r_2s_1) = \rho'_{21}(r_2s_2) + \rho'_{21}(r_1s_2) = \lambda_1\lambda_2\rho'(r, s),$$

where  $\rho(r, s)$  and  $\rho'(r, s)$  are defined by (8.01) and (8.03).

By means of these relations we may reduce the expressions for  $\alpha'_0$  and  $\beta'_0$  to a much simpler form. Our operations may be performed on the actual determinants which express the general solution, but they could, of course, be equally well described as transformations of the general equations (5.08)–(5.11).

First considering  $\nabla (\delta_{rs}\alpha_{rs})$ , we add to the  $m^{\text{th}}$  column on the right (m>0) the corresponding column (-m) on the left of the centre; the new element on the right is now given by the equations

(8.05) 
$$(m > 0, n \ge 0)$$
  $\delta_{mn}(\alpha_{mn} + \alpha_{-mn}) = \frac{m}{\nu_0} A_0 \delta_{mn} N_{mn} \{ \rho_{11}(m_1 n_1) + \rho_{12}(m_1 n_1) + \rho_{12}(m_2 n_1) \},$   

$$= \frac{m}{\nu_0} A_0 \delta_{mn} N_{mn} (\lambda_1^2 + \lambda_1 \lambda_2) \rho(m, n)$$

$$= \lambda_1 \frac{m}{\nu_0} A_0 \delta_{mn} N_{mn} \rho(m, n),$$

(8:06) 
$$(m > 0, s \le 0)$$
  $\delta_{mn} (\alpha_{mn} + \alpha_{-mn}) = -\lambda_2 \frac{m}{\nu_0} A_0 \delta_{mn} N_{mn} \rho (m, n).$ 

We next add  $\lambda_2/\lambda_1$  times the  $n^{\text{th}}$  row (n > 0) to the  $(-n)^{\text{th}}$  row; the elements of the negative rows  $(n \le 0)$  thus acquire the following values:—

$$(8.07) \ (m > 0, \ n \leqslant 0) \ \delta_{mn} \left\{ a_{mn} + a_{-mn} + \frac{\lambda_2}{\lambda_1} (a_{m-n} + a_{-m-n}) \right\} = 0 \ a_{00} = -\frac{m}{\nu_0} A_0 N_{00} \rho_{12} (0_1 0_1),$$

$$(8.08) (m \leq 0, n \leq 0) \delta_{mn} \left( \alpha_{mn} + \frac{\lambda_2}{\lambda_1} \alpha_{m-n} \right) = -\frac{m}{\nu_1} A_0 \delta_{mn} N_{mn} \rho_{12} (r_1 s_1).$$

These transformations do not alter the value of  $\nabla (\delta_{mn}a_{mn})$ , nor of  $\nabla' (\delta_{mn}a_{mn})$  when applied to this determinant, which continues to be identical with the principal minor of  $\nabla$  in its new form. Since in each of these determinants the elements of one entire quadrant  $(m > 0, n \le 0)$  are all zero, they may be expressed as the product of the two simply infinite determinants formed by the quadrants (m > 0, n > 0) and  $(m \le 0, n \le 0)$ . The former quadrant, however, is the same for  $\nabla$  and  $\nabla'$ , so that (5.35) may be written (after a little reduction\*) in the form

(8.09) 
$$\alpha'_{0} = -\lambda_{1}\lambda_{2} \sum_{0}^{\infty} (\alpha_{r} - \alpha_{-r}) = -\frac{27}{\pi\nu_{0} m A_{0} K'_{12}(0)} \frac{\nabla'_{0}}{\nabla_{0}},$$

where  $\nabla'_0$  is the principal minor of  $\nabla_0$ , the general elements  $\alpha'_{mn}$  of which is given by the equations

(8.10) 
$$a'_{mn} = \delta_{mn} \frac{27\rho_{12}(m,n)}{\pi\nu_1\nu_2 2^{m+n+2} (m+\frac{3}{2})_{m+1} (n+\frac{3}{2})_{n+1} K'_{12}(0)},$$

so that

(8.11) 
$$a'_{00} = 1$$
  $a'_{m0} = \delta_{m0} 2^{-m} \sum_{0}^{m} {}_{m} C_{t} k_{t} = a'_{0m}.$ 

Here, since  $m_1 = m_2$ , the equation (4.08) takes the special form

$$(8.12) \frac{\rho_{12}(r_{1}s_{1})}{\nu_{1}\nu_{2}}$$

$$= \frac{1}{3} \int \int e^{-x^{2}-y^{2}} x^{2} y^{2} \sum_{0}^{r+1,s+1} \left[\phi^{k}(y) \left\{ B^{k}(r+1,s) + B^{k}(r,s+1) \right\} + 2y^{2} \psi^{k}(y) B^{k}(r,s) \right] dx dy,$$

whence it is clear that  $\nabla_0$ , and consequently also  $\alpha'_0$ , is independent of the ratio  $\nu_1 : \nu_2$  (i.e.,  $\nu_1$  and  $\nu_2$  occur only in the form  $\nu_1 + \nu_2$  or  $\nu_0$ ).

It may readily be verified that a corresponding calculation in the case of  $\nabla \left(\delta_{mn}b_{mn}\right)$  leads to the result

$$\beta'_0 = 0.$$

In the same way we may determine the particular forms assumed by (5.37), (5.39), and (5.40) in this special case.

<sup>\*</sup> This reduction chiefly consists in cancelling out factors common to all the elements of corresponding rows of  $\nabla_0$  and  $\nabla'_0$ .

#### § 9. First and Second Approximations in the General Case.

#### (a) General Remarks.

In the general case there are no such simplifications as have been described in § 7-9, and for practical numerical purposes we have to be content with successive approximations to the complete solution. The approximate formulæ become increasingly complicated with each successive step, however, so that it is fortunate that a first or second approximation generally gives a close approach to accuracy. In the theory of viscosity and conduction in a simple gas ('Phil. Trans.,' A, vol. 216, § 11, p. 334) it was found that a first approximation gave a result not more than 2 or 3 per cent. too small, while the error after a second approximation was negligible. present theory of a composite gas the error of the first approximation may be much larger (up to 13 per cent.) in extreme cases where the masses, densities, or diameters of the two sets of molecules differ widely  $(cf. \S 7)$ . Such a case is worked out to a fifth approximation in  $\S 13$  (e), and as this is one in which an exact solution is possible by another method, the results there obtained throw much light on the general character of the convergence of our analysis. It would seem that (as in the previous memoir just cited) the successive approximations form a monatomic sequence, the first and second members of which give a good indication of the accurate limiting value. If the difference between these two members is about 2 per cent., the additional correction due to all further approximations is about \frac{1}{2} per cent., while if the difference is so much as 8 per cent., the further correction is about 4 per cent., the additional correction being in an increasing ratio to the first difference as the value of the latter rises.

In this paper we shall not go beyond a first approximation in the general case, except in regard to  $\alpha'_0$ , where we shall stop at the second approximation.

# (b) First Approximation to $\alpha'_0$ .

If in our set of equations (5.08) we neglect all save the central one, and consider only the central term of that, we get the equation

(9.01) 
$$a_{00}(\alpha_0 - \alpha_{-0}) = 1$$
, or  $a_{00}\alpha'_0 = -\lambda_1\lambda_2$ .

By (5.12) and (4.27) we have

(9.02) 
$$a_{00} = A_0 \frac{2\pi\nu_1\nu_2m_1m_2K'_{12}(0)}{27\nu_0(m_1+m_2)}.$$

It is convenient to choose A<sub>0</sub> (which is quite arbitrary as yet) so as to make

$$(9.021) a_{00} = 1,$$

so that

(9.022) 
$$A_{0} = \frac{27 (m_{1} + m_{2})}{2\pi \lambda_{1} \lambda_{2} \nu_{0} m_{1} m_{2} K'_{12}(0)},$$

and so that the equation for the first approximation to  $\alpha'_0$  becomes (with this value of  $A_0$ )

$$\alpha'_{0} = -\lambda_{1}\lambda_{2}.$$

#### (c) Second Approximation to $\alpha'_0$ .

We may conveniently obtain our second approximation by means of (5.35), taking the three rows and columns of  $\nabla$  and  $\nabla'$  which contain  $\alpha_{00}$  in the centre. From (5.12)–(5.14) it is easy to see that the elements have the following values (when  $\alpha_{00} = 1$ ):—

$$(9.04) \quad \delta_{01}a_{01} = \mu_2(k_1 - 1) = \delta_{10}a_{10} \equiv p_1, \quad \delta_{0-1}a_{0-1} = \mu_1(k_1 - 1) = -\delta_{-10}a_{-10} \equiv -p_2,$$

$$(9.05) \delta_{11}a_{11} = \left\{ \frac{6}{5}\mu_1^2 + \mu_2^2 \left(1 - 2k_1 + \frac{7}{5}k_2\right) + \frac{8}{25}\mu_1\mu_2k_{12}^0 + \frac{2}{25}\frac{\nu_1}{\nu_2\mu_2}k_{11}^0 \right\} \equiv p_{11},$$

$$(9.06) \quad \delta_{-1-1}a_{-1-1} = -\left\{ \frac{6}{5}\mu_{2}^{2} + \mu_{1}^{2} \left(1 - 2k_{1} + \frac{7}{5}k_{2}\right) + \frac{8}{25}\mu_{1}\mu_{2}k_{12}^{0} + \frac{2}{25}\frac{\nu_{2}}{\nu_{1}\mu_{1}}k_{22}^{0} \right\} \equiv -p_{22},$$

$$(9.07) \delta_{1-1}a_{1-1} = -\delta_{-11}a_{-11} = \mu_1\mu_2 \left\{ \frac{1}{5} - 2k_1 + \frac{7}{5}k_2 - \frac{8}{25}k_{12}^{0} \right\} \equiv -p_{12}.$$

Consequently, the third-order determinant for  $\nabla$  is given by

and its principal minor by

$$(9.081) - p_{12} p_{11} = -(p_{12}^2 - p_{11} p_{22}).$$
 
$$p_{22} p_{12}$$

It is easy to prove that

$$(9.082) (p_{12}^2 - p_{11}p_{22}) = -\frac{1}{2.5} \frac{1}{\nu_1 \nu_2} (d_1 \nu_1^2 + 2d_{12} \nu_1 \nu_2 + d_2 \nu_2^2),$$

where

$$(9.09) d_1 \equiv \frac{1}{\mu_2} k_{11}^{-0} \left\{ \frac{1}{5} \left( 1 - 2\mu_1 \mu_2 \right) + \frac{1}{2} \frac{6}{5} \mu_1 \mu_2 k_{12}^{-0} - 2 \left( \frac{1}{5} + 2k_1 - \frac{7}{5} k_2 \right) \mu_1^{-2} \right\},$$

$$(9.10) d_2 \equiv \frac{1}{4} k_{22} \left\{ \frac{1}{5} \left( 1 - 2\mu_1 \mu_2 \right) + \frac{1}{2} \frac{6}{5} \mu_1 \mu_2 k_{12} - 2 \left( \frac{1}{5} + 2k_1 - \frac{7}{5} k_2 \right) \mu_2^2 \right\},$$

$$(9.11) \quad 2d_{12} \equiv \frac{1}{2^{4}5} \frac{1}{\mu_{1}\mu_{2}} k_{11}{}^{0}k_{22}{}^{0} + \frac{6}{5} \left(1 - 4\mu_{1}\mu_{2}\right) \left(1 - 2k_{1} + \frac{7}{5}k_{2}\right) + 8\mu_{1}\mu_{2}k_{12}{}^{0} \left(\frac{1}{5} - 2k_{1} + \frac{7}{5}k_{2}\right).$$

Also

$$(9.12) 2p_1p_2p_{12}-p_{11}p_2^2-p_{22}p_1^2=-\frac{(k_1-1)^2}{25\nu_1\nu_2}(b_1\nu_1^2+2b_{12}\nu_1\nu_2+b_2\nu_2^2),$$

where

$$(9.13) b_1 = 2\mu_1\mu_{12}k_{11}^0, b_2 = 2\mu_2\mu_{21}k_{22}^0, 2b_{12} = 30(1 - 4\mu_1\mu_2) + 8\mu_1\mu_2k_{12}^0.$$

Consequently, if we write

(9.14) 
$$\epsilon_0 \equiv \frac{2p_1p_2p_{12} - p_{11}p_2^2 - p_{22}p_1^2}{p_{12}^2 - p_{11}p_{22}} = (k_1 - 1)^2 \frac{b_1\nu_1^2 + 2b_{12}\nu_1\nu_2 + b_2\nu_2^2}{d_1\nu_1^2 + 2d_{12}\nu_1\nu_2 + d_2\nu_2^2},$$

we have, as our second approximation to  $\alpha'_0$  by (5.35),

(9.15) 
$$\alpha'_{0} = -\lambda_{1}\lambda_{2}\frac{1}{1-\epsilon_{0}}.$$

We may note that

$$\Delta_{1} = \frac{1}{\nu_{1}\nu_{2}} \left\{ d_{1}\nu_{1}^{2} + 2d_{12}\nu_{1}\nu_{2} + d_{2}\nu_{2}^{2} \right\} - (k_{1} - 1)^{2} \left( b_{1}\nu_{1}^{2} + 2b_{12}\nu_{1}\nu_{2} + b_{2}\nu_{2}^{2} \right) \right\}$$

$$= \frac{1}{\nu_{1}\nu_{2}} \left\{ \alpha_{1}\nu_{1}^{2} + 2\alpha_{12}\nu_{1}\nu_{2} + \alpha_{2}\nu_{2}^{2} \right\},$$

where

(9.161) 
$$a_1 = \frac{2}{\mu_2} k_{11}^0 \left\{ \frac{6}{5} \mu_2^2 - \mu_1^2 \left( k_1^2 - \frac{7}{5} k_2 \right) + \frac{8}{25} \mu_1 \mu_2 k_{12}^0 \right\},$$

(9.162) 
$$a_2 = \frac{2}{\mu_1} k_{22} \left\{ \frac{6}{5} \mu_1^2 - \mu_2^2 \left( k_1^2 - \frac{7}{5} k_2 \right) + \frac{8}{2} \frac{1}{5} \mu_1 \mu_2 k_{12} \right\},$$

$$(9.163) a_{12} = d_{12} - (k_1 - 1)^2 b_{12}.$$

The determinant  $\nabla_0 (\delta_{mn} \alpha_{mn})$  of (5.37) is, to the same order of approximation as for  $\nabla (\delta_{mn} \alpha_{mn})$  in (9.08),

where

$$(9.17) \qquad \epsilon_1 \equiv 30 \left( \nu_1 \mu_2 + \nu_2 \mu_1 \right) \left( \mu_1 - \mu_2 \right) - 8 \mu_1 \mu_2 k^0_{12} \left( \nu_1 - \nu_2 \right) + 2 \left( \nu_1 \mu_{12} k^0_{11} - \nu_2 \mu_{21} k^0_{22} \right).$$

Hence we have, as a first approximation,

(9.18) 
$$\sum_{1}^{\infty} r \left( \nu_1 \alpha_r + \nu_2 \alpha_{-r} \right) = \frac{k_1 - 1}{\Delta_1} \epsilon_1.$$

## (d) First Approximation to $\beta'_{0}$ and $\sum (\nu_{1}\beta_{\tau} - \nu_{2}\beta_{-\tau})$ .

In this case, owing to the fact that the central element in the numerator determinants of (5:36) and (5:39) is zero, we have to deal with the third order determinant in order to obtain a first approximation. From (5:15)-(5:18) it is easy to see that  $\nabla (\delta_{mn}b_{mn})$  may be obtained from  $\nabla (\delta_{mn}a_{mn})$ , each being limited to the three central rows and columns, if we replace  $a_{00}$  by  $\frac{B_0}{A_0R}a_{00}$ , and divide the top and bottom rows respectively by  $\lambda_1$  and  $-\lambda_2$ . Consequently the third order determinant obtained from  $\nabla (\delta_{mn}b_{mn})$  is equal to  $-\frac{1}{2\cdot 5}\frac{1}{\lambda_1\lambda_2}\left(\frac{B_0}{A_0R}\right)^3\Delta_1$ . The value of  $\nabla'_0(\delta_{mn}b_{mn})$  is similarly  $(cf. \S 5 (f))$  for the definition of this determinant),

$$(9.19) \quad \left(\frac{\mathbf{B}_{0}}{\mathbf{A}_{0}\mathbf{R}}\right)^{2} \quad \frac{p_{12}}{\lambda_{1}} \quad 1 \quad \frac{p_{11}}{\lambda_{1}} \quad = \frac{1}{\lambda_{1}\lambda_{2}\nu_{0}} \left(\frac{\mathbf{B}_{0}}{\mathbf{A}_{0}\mathbf{R}}\right)^{2} \quad p_{12} \quad \nu_{1} \quad p_{11} \quad = -\frac{k_{1}-1}{25\lambda_{1}\lambda_{2}\nu_{0}} \left(\frac{\mathbf{B}_{0}}{\mathbf{A}_{0}\mathbf{R}}\right)^{2} \boldsymbol{\epsilon}_{1}$$

$$p_{2} \quad 0 \quad p_{1} \quad p_{22} \quad \nu_{2} \quad p_{12}$$

$$p_{22} \quad \nu_{2} \quad p_{12}$$

by (9.17). Hence, by (5.36), we have

(9.20) 
$$\beta'_{0} = -\frac{A_{0}R}{B_{0}} \frac{k_{1}-1}{\nu_{0}\Delta_{1}} \lambda_{1} \lambda_{2} \epsilon_{1} = -\frac{A_{0}R}{B_{0}} \frac{\lambda_{1}\lambda_{2}}{\nu_{0}} \sum_{1}^{\infty} r (\nu_{1}\alpha_{\tau} + \nu_{2}\alpha_{-\tau})^{*}$$
by (9.18).

Again, the determinant  $\nabla_0 (\delta_{mn} b'_{mn})$  defined in § 5 (g) has the form

$$(9.21) \quad \left(\frac{\mathbf{B}_{0}}{\mathbf{A}_{0}\mathbf{R}}\right)^{2} \qquad \frac{1}{2} \left(\frac{p_{12}}{\lambda_{1}} - \frac{p_{22}}{\lambda_{2}}\right) - p_{2} \qquad \frac{1}{2} \left(\frac{p_{11}}{\lambda_{1}} - \frac{p_{22}}{\lambda_{2}}\right) - 1 \qquad \frac{1}{2} \left(\frac{p_{11}}{\lambda_{1}} - \frac{p_{12}}{\lambda_{2}}\right) - p_{1}$$

$$= \frac{1}{2} \left(\frac{p_{12}}{\lambda_{1}} - \frac{p_{22}}{\lambda_{2}}\right) - p_{2} \qquad -\frac{1}{2} \left(\frac{p_{1}}{\lambda_{1}} - \frac{p_{2}}{\lambda_{2}}\right) - 1 \qquad -\frac{1}{2} \left(\frac{p_{11}}{\lambda_{1}} - \frac{p_{12}}{\lambda_{2}}\right) - p_{1}$$

$$= \left(\frac{\mathbf{B}_{0}}{\mathbf{A}_{0}\mathbf{R}}\right)^{2} \qquad \qquad p_{2} \qquad \qquad 1 \qquad \qquad p_{1}$$

$$= \frac{p_{12}}{\lambda_{1}} - \frac{p_{22}}{\lambda_{2}} \qquad \frac{p_{1}}{\lambda_{1}} - \frac{p_{2}}{\lambda_{2}} \qquad \frac{p_{11}}{\lambda_{1}} - \frac{p_{12}}{\lambda_{2}}$$

$$= -\frac{\nu_{0}}{\nu_{1}\nu_{2}} \left(\frac{\mathbf{B}_{0}}{\mathbf{A}_{0}\mathbf{R}}\right)^{2} \left[\nu_{1}^{2} \left(p_{22} - p_{2}^{2}\right) + 2\nu_{1}\nu_{2} \left(p_{12} - p_{1}p_{2}\right) + \nu_{2}^{2} \left(p_{11} - p_{1}^{2}\right)\right]$$

$$= -\frac{\nu_{0}}{2\nu_{1}\nu_{2}} \left(\frac{\mathbf{B}_{0}}{\mathbf{A}_{0}\mathbf{R}}\right)^{2} \left[\frac{\mu_{2}}{k_{11}^{0}} a_{1}\nu_{1}^{2} + 2a'_{12}\nu_{1}\nu_{2} + \frac{\mu_{1}}{k_{22}^{0}} a_{2}\nu^{2}\right],$$

<sup>\*</sup> This last equation, here proved true only by comparing the first approximations to  $\beta'_0$  and  $\Sigma r(\nu_1\alpha_r + \nu_2\alpha_{-r})$ , may easily be shown to be strictly accurate, by comparing the general expressions for these quantities.

where  $a_1$  and  $a_2$  are given by (9.161), (9.162) and  $a'_{12}$  by

$$a'_{12} = \mu_1 \mu_2 \left\{ \frac{6}{5} - k_1^2 + \frac{7}{5} k_2 - \frac{8}{25} k_{12}^0 + \frac{1}{25} \left( \frac{k_{11}^0}{\mu_2} + \frac{k_{22}^0}{\mu_1} \right) \right\}.$$

Consequently, by (5.39), to this order of approximation we have

(9.23) 
$$\sum_{1}^{\infty} (\nu_{1}\beta_{\tau} + \nu_{2}\beta_{-\tau}) = \frac{25 A_{0} R}{2 B_{0} \nu_{0} \nabla_{1}} \left\{ \frac{\mu_{2}}{k_{11}^{0}} \alpha_{1} \nu_{1}^{2} + 2 \alpha'_{12} \nu_{1} \nu_{2} + \frac{\mu_{1}}{k_{22}^{0}} \alpha_{2} \nu_{2}^{2} \right\}.$$

(e) The First Approximation to  $\Sigma(\nu_1\gamma_r + \nu_2\gamma_{-r})$ .

The two central terms of the two central equations of type (5.11) are

$$(9.24) \qquad \gamma_0 \left\{ 1 + \frac{3}{10} \mu_{21} k_{12}^0 + \frac{3}{20} \frac{\nu_1}{\nu_2} \frac{1}{\mu_1 \mu_2} k_{11}^0 \right\} - \gamma_{-0} \left( 1 - \frac{3}{10} k_{12}^0 \right) = \frac{675 \nu_1}{8 \pi \nu_1 \nu_2 \mu_1 \mu_2} C_0 K'_{12}(0),$$

$$(9.25) \quad -\gamma_0 \left(1 - \frac{3}{10} k_{12}^{0}\right) + \gamma_{-0} \left\{1 + \frac{3}{10} \mu_{12} k_{12}^{0} + \frac{3}{20} \frac{\nu_2}{\nu_1} \frac{1}{\mu_1 \mu_2} k_{22}^{0}\right\} \stackrel{\cdot}{=} \frac{675 \nu_2}{8 \pi \nu_1 \nu_2 \mu_1 \mu_2 C_0 K'_{12}(0)},$$

which lead to the result (equivalent to that obtained as a first approximation from 5.40),

(9.26) 
$$C_0 \sum_{0}^{\infty} (\nu_1 \gamma_r + \nu_2 \gamma_{-r}) = \frac{1125}{2\pi K'_{12}(0)} \frac{c_1 \nu_1^2 + 2c_{12} \nu_1 \nu_2 + c_2 \nu_2^2}{k_{11}^0 c_1 \nu_1^2 + 2k_{12}^0 c'_{12} \nu_1 \nu_2 + \frac{3}{20} k_{20}^2 c_2 \nu_2^2},$$

where

(9.27), (9.28) 
$$c_1 \equiv 1 + \frac{3}{10} \mu_{12} k_{12}^0$$
,  $c_2 = 1 + \frac{3}{10} \mu_{21} k_{12}^0$ ,

$$(9.29) c_{12} = 1 - \frac{3}{10} k_{12}^{0} + \frac{3}{40} \frac{1}{\mu_{1} \mu_{2}} (k_{11}^{0} + k_{22}^{0}),$$

$$(9.30) c'_{12} = 1 + \frac{3}{40} \frac{1}{\mu_1 \mu_2} \frac{k_{11}{}^0 k_{22}{}^0}{k_{12}{}^0}.$$

A second approximation would replace the right-hand factor in (9.26), by the quotient of one quartic homogeneous polynomial in  $\nu_1$ ,  $\nu_2$  by another, and similarly each further approximation would increase the degree of both numerator and denominator by 2.

# (f) Values of $K'_{12}(0)$ for Particular Molecular Models.

In connection with the above approximate formulæ, and their subsequent applications, it is convenient here to write down the values taken by  $K'_{12}(0)$  and the other constants k, when certain particular characteristics are attributed to the molecules.

When the molecules are regarded as rigid elastic spheres of radii  $\sigma_1$  and  $\sigma_2$ , it may readily be shown (cf. 'Phil. Trans.,' A, vol. 216, § 9, p. 320) that

(9.31) 
$$K'_{12}(0) = 4 \left(\sigma_1 + \sigma_2\right)^2 \left(\frac{m_1 + m_2}{h \pi m_1 m_2}\right)^{1/2},$$

$$(9.32) k_t = \frac{(t+2)_t}{(t+\frac{3}{2})_t} k_{11}^t = \left(\frac{2\sigma_1}{\sigma_1 + \sigma_2}\right)^2 k_{12}^t k_{22}^t = \left(\frac{2\sigma_2}{\sigma_1 + \sigma_2}\right)^2 k_{12}^t k_{12}^t = \frac{5}{3} \frac{(t+3)_{t+1}}{(t+\frac{5}{2})_{t+1}}.$$

When the molecules are point centres of force proportional to the inverse  $n^{\text{th}}$  power of the distance, the force at unit distance being  $K_{12}m_1m_2$ , it may be shown\* that

(9.33) 
$$K'_{12}(0) = \frac{2}{\pi^{\frac{3}{l_2}}} I_1(n) \left( \frac{h m_1 m_2}{m_1 + m_2} \right)^{\frac{2}{n-1} - \frac{1}{l_2}} \left[ K_{12}(m_1 + m_2) \right]^{\frac{2}{n-1}} \Gamma\left( 3 - \frac{1}{n-1} \right),$$

where

(9.34) 
$$I_{1}(n) \equiv 4\pi \int_{0}^{\infty} \sin^{2}\frac{1}{2}\theta \cdot \alpha \, d\alpha$$

and

(9.35) 
$$\pi - \theta = 2 \int_0^{\eta_0} \frac{d\eta}{\sqrt{\left\{1 - \eta^2 - \frac{2}{n-1} \left(\frac{\eta}{\alpha}\right)^{n-1}\right\}}},$$

 $\eta_0$  being the root of the following equation in  $\eta$ :

$$(9.36) 1 - \eta^2 - \frac{2}{n-1} \left(\frac{\eta}{\alpha}\right)^{n-1} = 0.$$

Further,

$$(9.37) k_{t} = \frac{\Gamma\left(t+3-\frac{2}{n-1}\right)}{(t+\frac{3}{2})_{t}\Gamma\left(3-\frac{2}{n-1}\right)} k_{12}^{t} = 5 \frac{\Gamma\left(t+4-\frac{2}{n-1}\right)}{(t+\frac{5}{2})_{t+1}\Gamma\left(3-\frac{2}{n-1}\right)} \frac{I_{2}(n)}{I_{1}(n)},$$

where

(9.38) 
$$I_2(n) = \pi \int_0^\infty \sin^2 \theta \cdot \alpha \, d\alpha.$$

Also

$$(9.39) k_{11}^{t} = \left(\frac{\mathbf{K}_{11}}{\mathbf{K}_{12}}\right)^{\frac{2}{n-1}} k_{12}^{t} k_{22}^{t} = \left(\frac{\mathbf{K}_{22}}{\mathbf{K}_{12}}\right)^{\frac{2}{n-1}} k_{12}^{t},$$

where  $K_{11}$ ,  $K_{22}$  are the force constants appropriate to a pair of molecules of the first or second kind respectively; we here assume that the law of variation of force with distance is the same whether the molecules are like or unlike—if this be not so, n must

<sup>\*</sup> Cf. 'Phil. Trans.,' A, vol. 216, § 9, p. 320, or Jeans' Dynamical Theory of Gases' (2nd edit.), §§ 305 et seq. I have adopted the notation of the above equations in order to facilitate comparison with the corresponding equations in Jeans' treatise.

also have suffixes 11, 12, or 22, and the formulæ (9.37)-(9.39) will need to be modified in a manner sufficiently obvious.

When n = 5, i.e., when the molecules are Maxwellian, it is clear that

(9.40) 
$$K'_{12}(0) = \frac{3}{2\pi} I_1(5) [K_{12}(m_1 + m_2)^{1/2}],$$

(9.41) 
$$k_t = 1 k_{12}^t = 5 \frac{I_2(5)}{I_1(5)}.$$

§ 10. The Equation of Diffusion.

(a) Definitions of the Various Coefficients of Diffusion.

In our analysis of molecular motions (§ 1) the rate of inter-diffusion was expressed in terms of  $u'_0$ , which is defined by the equations

(10.01) 
$$(\nu_1 + \nu_2) u'_0 = \nu_1 (u_1 - u_0) = -\nu_2 (u_2 - u_0) = \frac{\nu_1 \nu_2}{\nu_1 + \nu_2} (u_1 - u_2).$$

Further, by (3.15) and (2.06), we have, as the equation of diffusion,

(10.02) 
$$u_0' = \frac{1}{9} A_0 \alpha_0' \left( \frac{1}{2h} \frac{\partial \lambda_0'}{\partial x} - X_0' - \frac{m_0'}{\nu_0 m_0} \frac{\partial p_0}{\partial x} \right) + \frac{1}{9} B_0 \beta_0' \frac{\partial T}{\partial x}.$$

Hence it appears that the agents effective in causing diffusion are (taking the terms of this equation in order) a concentration-gradient or variation in the relative proportions of the two component gases, external forces of unequal amounts per unit mass of the two gases, and variations in the total pressure or the temperature of the composite gas.

When the pressure and temperature are uniform, and the external forces are such as to make  $X'_0$ ,  $Y'_0$ ,  $Z'_0$  zero, diffusion can take place only if there is a variation in the relative concentration of the component gases. In this case we may compare (10.02) which now has the special form

(10.03) 
$$u_0' = \frac{1}{9} A_0 \alpha_0' \frac{1}{2h} \frac{\partial \lambda_0'}{\partial x} = \frac{1}{9\nu_0} A_0 \alpha_0' \frac{1}{2h} \frac{\partial \nu_1}{\partial x} = -\frac{1}{9\nu_0} A_0 \alpha_0' \frac{1}{2h} \frac{\partial \nu_2}{\partial x},$$

with the ordinary equation of diffusion

(10.04) 
$$\nu_0 u'_0 = \nu_1 (u_1 - u_0) = -D_{12} \frac{\partial \nu_1}{\partial x} \qquad \nu_2 (u_2 - u_0) = -D_{12} \frac{\partial \nu_2}{\partial x},$$

where  $D_{12}$  is the coefficient of diffusion. By comparison we have

(10.05) 
$$D_{12} = -\frac{1}{9} A_0 RT \alpha'_0.$$

When the pressure, temperature, and composition of the gas are uniform, a steady motion of diffusion may be produced by equal and opposite forces  $\pm (\nu_0 X'_0, \nu_0 Y'_0, \nu_0 Z'_0)$  per unit volume on the two components. This will be termed forced diffusion, and we define the coefficient of forced diffusion  $D'_{12}$  by the equation

$$(10.06) u_0' = D_{12}^{\prime} v_0 X_0',$$

so that, by comparison with (10.02),

(10.07) 
$$D'_{12} = -\frac{1}{9} \frac{1}{\nu_0} A_0 \alpha'_0 = \frac{1}{p_0} D_{12}.$$

From (10.02) it is clear that diffusion will occur also when the relative proportion of the two gaseous components is uniform, and in the absence of external forces such as might produce diffusion, provided that the pressure or temperature varies. If we define coefficients of thermal diffusion  $D_T$  and of pressure diffusion  $D_p$  by the equation

(10.08) 
$$u_0' = D_p \frac{1}{p_0} \frac{\partial p_0}{\partial x} - D_T \frac{1}{T} \frac{\partial T}{\partial x},$$

we have, by comparison with (10.02)

(10.09) 
$$D_{p} = -\frac{1}{9} A_{0} \alpha'_{0} \frac{p_{0} m'_{0}}{\nu_{0} m_{0}} = -\frac{1}{9} A_{0} R T \alpha'_{0} \frac{m'_{0}}{m_{0}} = \frac{m'_{0}}{m_{0}} D_{12},$$

(10.10) 
$$D_{T} = -\frac{1}{9}B_{0}\beta'_{0}T.$$

(b) The Equation of Diffusion.

If we now substitute the various coefficients of diffusion in the equation of diffusion (10.02), this becomes

(10.11) 
$$u_0' = -D_{12} \frac{\partial \lambda_0'}{\partial x} + D_{12} \nu_0 X_0' + D_p \frac{1}{p_0} \frac{\partial p_0}{\partial x} - D_T \frac{1}{T} \frac{\partial T}{\partial x}.$$

In later sections, when we consider in detail the values of the four coefficients of diffusion, we shall see that they are all positive (the molecules 1 being the heavier—cf. §1).\* Hence from (10·11) we deduce that the direction of diffusion of the heavier component of a gas is (a) opposite to the direction of increasing concentration (b) in the direction of the diffusion-component of the external force (c) in the direction of increasing mean pressure and (d) opposite to the direction of increasing temperature.\* This is fairly evident as regards (a) and (b). In case (c), the sign of  $D_p$  is the same as that of  $m'_0$  (cf. (10·09),  $D_{12}$  being always positive), which is a multiple of  $m_1-m_2$ ; the physical reason is also not difficult to grasp—under the influence of a difference of pressure both components will tend to flow in the direction of diminishing pressure, so as to render the pressure uniform. The lighter molecules will travel

\* This statement is modified, with regard to D<sub>T</sub>, in Note E, p. 197.

faster than the heavier, however, so that relative to the mean motion the heavier gas will be diffusing in the direction of increasing pressure. Such a process must go on, to some extent, during the passage of sound-waves in air or any mixed gas, and will influence the propagation of the disturbance to a degree which is probably comparable with that of the effects due to viscosity and thermal conduction. The effects of these latter have been examined by Stokes, Kirchhoff, and Rayleigh.\*

It is rather more difficult to perceive, either analytically or physically, that  $D_T$  must be positive if the molecules 1 are the heavier (see Note E, p. 197). A discussion of this coefficient will be found in §14.

If in (10.11) we assign to  $u'_0$  the value zero, we get the equation of condition for a state without diffusion. Some special cases of this equation will be considered in §16, after the relative magnitudes of the various coefficients of diffusion have been determined.

# § 11. THE EQUATION OF VISCOSITY.

The various pressure components  $p_{xx}$ ,  $p_{xy}$ , et cetera, for the composite gas are given by the following and similar equations:—

(11.01) 
$$p_{xx} = \nu_1 m_1 \overline{\mathsf{U}_1}^2 + \nu_2 m_2 \overline{\mathsf{U}_2}^2, \qquad p_{xy} = \nu_1 m_1 \overline{\mathsf{U}_1} \mathsf{V}_1 + \nu_2 m_2 \overline{\mathsf{U}_2} \mathsf{V}_2.$$

A reference to (5.24) or to our expressions for f(U, V, W) in §3 hence enables us to deduce that

(11.02) 
$$p_{zz}-p_0 = -\frac{4}{675} \frac{1}{2h} C_0 c_{zz} \sum_{0}^{\infty} (\nu_1 \gamma_r + \nu_2 \gamma_{-r}),$$

(11.03) 
$$p_{xy} = -\frac{4}{675} \frac{1}{2h} C_0 c_{xy} \sum_{0}^{\infty} (\nu_1 \gamma_r + \nu_2 \gamma_{-r}),$$

We may compare these with the equations of pressure of a gas whose coefficient of viscosity is  $\kappa_{12}(cf. (2.11) \text{ and } (2.14) \text{ for the values of } c_{xx} \text{ and } c_{xy}) :—$ 

$$(11.04) p_{xx} - p_0 = -\kappa_{12} \left[ 2 \frac{\partial u_0}{\partial x} - \frac{2}{3} \left( \frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial 2} \right) \right] = -\frac{2}{3} \kappa_{12} c_{xx},$$

(11.05) 
$$p_{xy} = -\kappa_{12} \left( \frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y} \right) = -\frac{2}{3} \kappa_{12} c_{xy}.$$

It thus becomes evident that the composite gas behaves like a viscous fluid whose coefficient of viscosity is given by

(11.06) 
$$\kappa_{12} = \frac{2}{22.5} \frac{C_0}{2h} \sum_{0}^{\infty} (\nu_1 \gamma_r + \nu_2 \gamma_{-r}).$$

\* STOKES, 'Cambridge Transactions,' 8, p. 287, 1845; KIRCHHOFF, 'Pogg. Ann.,' 134, p. 177, 1868; RAYLEIGH, 'Phil. Trans.,' 175, p. 1883, 'Theory of Sound,' II., ch. XIX.

§ 12. The Equation of Energy.

(a) The Deduction of the Equation.

In order to obtain the equation of energy we return to the consideration of the equation of transfer (2.01). Having determined the form of the velocity distribution function f(U, V, W) correct to the first order of small quantities, we can now make the equations of transfer accurate so far as the second order, and this is necessary in connection with the equation of energy. Also we need no longer suppose that the mean motion of the gas  $(u_0, v_0, w_0)$  at the point considered is zero.

We add to (2.01) the corresponding equation for the molecules of the second kind, with the result

$$(12.01) \quad \frac{\partial}{\partial t} \left(\nu_{1}\overline{Q_{1}} + \nu_{2}\overline{Q_{2}}\right) + \sum_{xyz} \left[\frac{\partial}{\partial \boldsymbol{x}} \left\{\nu_{1} \left(\overline{u}\right)_{1}\overline{Q_{1}} + \nu_{2} \left(\overline{u}\right)_{2}\overline{Q_{2}}\right\} - \left\{\frac{\nu_{1}}{m_{1}} X_{1} \left(\overline{\frac{\partial Q_{1}}{\partial \left(u\right)_{1}}}\right) + \frac{\nu_{2}}{m_{2}} X_{2} \left(\overline{\frac{\partial Q_{2}}{\partial \left(u\right)_{2}}}\right)\right\}\right] = \Delta \left(Q_{1} + Q_{2}\right).$$

In this equation we substitute in turn Q = 1, Q = m(u), and  $Q = \frac{1}{2}m\{(u)^2 + (\nu)^2 + (w)^2\}$ , thus obtaining the equations of density, momentum, and energy. Since all three of these quantities are conserved unchanged during the molecular encounters, we have in each case  $\Delta(Q_1 + Q_2) = 0$ . The first equation takes the form

$$\frac{\partial \nu_0}{\partial t} + \frac{\partial \nu_0 u_0}{\partial x} + \frac{\partial \nu_0 v_0}{\partial y} + \frac{\partial \nu_0 w_0}{\partial z} = 0,$$

where we have made use of the notation of § 1. We will denote the operator

$$\frac{\partial}{\partial t} + u_0 \frac{\partial}{\partial x} + v_0 \frac{\partial}{\partial y} + w_0 \frac{\partial}{\partial z}$$

by  $\frac{D}{Dt}$ , commonly known as the "mobile operator"; if q is any function of x, y, z, t,  $\frac{D_q}{Dt}$  denotes the rate of change, with respect to time, if the value of q at a point which moves with the mean velocity of the gas. Then the equation of continuity (12.02) may also be written in the form

(12.03) 
$$\frac{1}{\nu_0} \frac{D\nu_0}{Dt} + \left( \frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} \right) = 0.$$

The second equation, the equation of momentum, may be written as

$$(12.04) \quad \frac{\partial}{\partial t} \left( \rho_1 u_1 + \rho_2 u_2 \right) + \frac{\partial}{\partial x} \left\{ \rho_1 \overline{\left(u\right)_1}^2 + \rho_2 \overline{\left(u\right)_2}^2 \right\} + \frac{\partial}{\partial y} \left\{ \rho_1 \overline{\left(u\right)_1} \overline{\left(v_1\right)} + \rho_2 \overline{\left(u\right)_2} \overline{\left(v_2\right)} \right\}$$
$$+ \frac{\partial}{\partial z} \left\{ \rho_1 \overline{\left(u\right)_1} \overline{\left(w\right)_1} + \rho_2 \overline{\left(u\right)_2} \overline{\left(w\right)_2} \right\} - \left(\nu_1 X_1 + \nu_2 X_2\right) = 0,$$

or (cf. § 1 and (11.01)) as

$$(12.05) \quad \nu_{0}X_{0} = \frac{\partial}{\partial t} \left( \rho_{0}u_{0} + \rho'_{0}u'_{0} \right) + \frac{\partial}{\partial x} \left\{ \rho_{0}u_{0}^{2} + 2\rho'_{0}u_{0}u'_{0} + p_{xx} \right\}$$

$$+ \frac{\partial}{\partial y} \left\{ \rho_{0}u_{0}v_{0} + \rho'_{0} \left( u_{0}v'_{0} + u'_{0}v_{0} \right) + p_{xy} \right\}$$

$$+ \frac{\partial}{\partial z} \left\{ \rho_{0}u_{0}w_{0} + \rho'_{0} \left( u_{0}w'_{0} + u'_{0}v_{0} \right) + p_{xx} \right\}$$

$$= \nu_{0} \frac{D}{Dt} \left\{ m_{0}u_{0} + \left( m_{1} - m_{2} \right) u'_{0} \right\} + \rho'_{0}u_{0} \left( \frac{\partial u'_{0}}{\partial x} + \frac{\partial v'_{0}}{\partial y} + \frac{\partial w'_{0}}{\partial z} \right)$$

$$+ \left( \frac{\partial p_{xx}}{\partial x} + \frac{\partial p_{xy}}{\partial y} + \frac{\partial p_{xz}}{\partial z} \right) + \left( u'_{0} \frac{\partial \rho'_{0}u_{0}}{\partial x} + v'_{0} \frac{\partial \rho'_{0}u_{0}}{\partial y} + w'_{0} \frac{\partial \rho'_{0}u_{0}}{\partial z} \right).$$

In deducing the third equation, the equation of energy, it is convenient, first of all, to write out the following equations giving the appropriate special values of the various quantities which occur in (12.01):—

(12.06) 
$$\nu_{1}\overline{Q_{1}} + \nu_{2}\overline{Q_{2}} = \frac{1}{2}\nu_{1}m_{1}\left(c_{0}^{2} + 2\frac{1}{\lambda_{1}}\sum u_{0}u'_{0} + \overline{C_{1}^{2}}\right) + \frac{1}{2}\nu_{2}m_{2}\left(c_{0}^{2} - 2\frac{1}{\lambda_{2}}\sum u_{0}u'_{0} + \overline{C_{2}^{2}}\right)$$
$$= \frac{1}{2}\rho_{0}c_{0}^{2} + \rho'_{0}\sum u_{0}u'_{0} + \frac{3}{2}R\nu_{0}T,$$

(12.07) 
$$\nu_{1} \overline{(u)_{1} Q_{1}} + \nu_{2} \overline{(u)_{2} Q_{2}} = u_{0} \left( \frac{1}{2} \rho_{0} c_{0}^{2} + {\rho'}_{0} \Sigma u_{0} u'_{0} + \frac{3}{2} R \nu_{0} T \right) + \frac{1}{2} {\rho'}_{0} u'_{0} {c_{0}}^{2} + (u_{0} p_{xx} + v_{0} p_{xy} + w_{0} p_{xz}) + (\frac{1}{2} \rho_{1} \overline{\mathsf{U}_{1} C_{1}}^{2} + \frac{1}{2} \rho_{2} \overline{\mathsf{U}_{2} C_{2}}^{2}),$$

(12.08) 
$$\frac{\nu_1}{m_1} X_1 \left( \frac{\partial Q_1}{\partial (u)_1} \right) + \frac{\nu_2}{m_2} X_2 \left( \frac{\partial Q_2}{\partial (u)_2} \right) = \nu_1 u_1 X_1 + \nu_2 u_2 X_2 = \nu_0 u_0 X_0 + \nu_0 u_0' (X_1 - X_2).$$

On substitution of these values in (12.01), this becomes

(12.09) 
$$\nu_{0} \frac{D}{Dt} \left\{ \frac{1}{2} m_{0} c_{0}^{2} + (m_{1} - m_{2}) \Sigma u_{0} u'_{0} + \frac{3}{2} RT \right\} + \frac{1}{2} \Sigma \frac{\partial}{\partial x} \left( \rho'_{0} c_{0}^{2} u'_{0} \right)$$

$$+ \Sigma \frac{\partial}{\partial x} \left( u_{0} p_{xx} + v_{0} p_{xy} + w_{0} p_{xz} \right) + \Sigma \frac{\partial}{\partial x} \left( \frac{1}{2} \rho_{1} \overline{\mathsf{U}_{1} C_{1}^{2}} + \frac{1}{2} \rho_{2} \overline{\mathsf{U}_{2} C_{2}^{2}} \right)$$

$$- \nu_{0} \Sigma u'_{0} \left( X_{1} - X_{2} \right) - \nu_{0} \Sigma u_{0} X_{0} = 0.$$

This equation can be simplified by eliminating  $\nu_0 \Sigma u_0 X_0$ ; thus from (12.05) we deduce that

(12.10) 
$$\nu_{0} \Sigma u_{0} X_{0} = \nu_{0} \frac{D}{Dt} \left( \frac{1}{2} m_{0} c_{0}^{2} \right) + \nu_{0} \Sigma u_{0} \frac{D}{Dt} \left( m_{1} - m_{2} \right) u'_{0} + \rho'_{0} c_{0}^{2} \left( \frac{\partial u'_{0}}{\partial x} + \frac{\partial v'_{0}}{\partial y} + \frac{\partial w'_{0}}{\partial z} \right)$$

$$\Sigma u_{0} \left( \frac{\partial p_{xx}}{\partial x} + \frac{\partial p_{xy}}{\partial y} + \frac{\partial p_{xx}}{\partial z} \right) + \frac{1}{2} \Sigma u'_{0} \frac{\partial \rho'_{0} c_{0}^{2}}{\partial x},$$

by means of which we may transform (12.09) into

$$(12.11) \quad \frac{3}{2} \operatorname{R}\nu_{0} \frac{\operatorname{DT}}{\operatorname{D}t} + \nu_{0} \left( m_{1} - m_{2} \right) \Sigma u'_{0} \frac{\operatorname{D}u_{0}}{\operatorname{D}t} - \frac{1}{2} \rho'_{0} c_{0}^{2} \left( \frac{\partial u'_{0}}{\partial x} + \frac{\partial v'_{0}}{\partial y} + \frac{\partial w'_{0}}{\partial z} \right) - \nu_{0} \Sigma u'_{0} \left( X_{1} - X_{2} \right)$$

$$+ \Sigma \left( p_{xx} \frac{\partial u_{0}}{\partial x} + p_{xy} \frac{\partial v_{0}}{\partial x} + p_{xz} \frac{\partial w_{0}}{\partial x} \right) + \Sigma \frac{\partial}{\partial x} \left( \frac{1}{2} \rho_{1} \overline{\operatorname{U}_{1} \operatorname{C}_{1}^{2}} + \frac{1}{2} \rho_{2} \overline{\operatorname{U}_{2} \operatorname{C}_{2}^{2}} \right) = 0.$$

In this equation we substitute the values of  $p_{xx}$ ,  $p_{xy}$ ,  $p_{xz}$  from (11.04), (11.05), et cetera. Also we divide throughout by J, the mechanical equivalent of heat, and replace  $\frac{3}{2} \frac{R}{Jm_0}$  by  $C_v$ , the specific heat of the gas at constant volume.\* After a little reduction we obtain the equation of energy in the following form:—

$$(12 \cdot 12) \quad \rho_{0} C_{v} \frac{DT}{Dt} + \frac{2}{3} \rho_{0} C_{v} T \left( \frac{\partial u_{0}}{\partial x} + \frac{\partial v_{0}}{\partial y} + \frac{\partial w_{0}}{\partial z} \right) = \frac{1}{J} \sum_{\nu_{0}} u'_{0} \left\{ \left( X_{1} - m_{1} \frac{Du_{0}}{Dt} \right) - \left( X_{2} - m_{2} \frac{Du_{0}}{Dt} \right) \right\}$$

$$+ \frac{1}{2} \frac{\nu_{0}}{J} \left( m_{1} - m_{2} \right) c_{0}^{2} \left( \frac{\partial u'_{0}}{\partial x} + \frac{\partial v'_{0}}{\partial y} + \frac{\partial w'_{0}}{\partial z} \right)$$

$$+ \frac{\kappa_{12}}{J} \left\{ 2 \sum_{v} \left( \frac{\partial u_{0}}{\partial x} \right)^{2} + \sum_{v} \left( \frac{\partial w_{0}}{\partial y} + \frac{\partial v_{0}}{\partial z} \right)^{2} - \frac{2}{3} \left( \sum_{v} \frac{\partial u_{0}}{\partial x} \right)^{2} \right\}$$

$$- \frac{1}{J} \sum_{v} \frac{\partial}{\partial x} \left( \frac{1}{2} \rho_{1} \overline{U_{1} C_{1}}^{2} + \frac{1}{2} \rho_{2} \overline{U_{2} C_{2}}^{2} \right).$$

## (b) The Interpretation of the Equation of Energy.

We will now consider the significance of the various terms in the equation of energy (12.12). The terms on the right depend on diffusion, viscosity, and thermal conduction (as will be made clearer later). If we neglect the small changes of energy produced by these means, as a first approximation (12.12) may be written

(12.13) 
$$\frac{1}{T}\frac{DT}{Dt} + \frac{2}{3}\left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}\right) = 0,$$

where we have omitted the right-hand side of (12.12), and divided the left hand by  $\rho_0 C_v T$ .

\* The specific heat of a simple gas at constant volume is  $\frac{3}{2} \frac{R}{Jm}$ , if m is the molecular mass (cf. Jeans' Dynamical Theory of Gases,' 2nd edit., § 261, (512)). Hence for a composite gas we have

$$\rho_0 \mathbf{C}_v \, = \, \tfrac{3}{2} \rho_1 \, \frac{\mathbf{R}}{\mathbf{J} m_1} + \tfrac{3}{2} \rho_2 \, \frac{\mathbf{R}}{\mathbf{J} m_2} \, = \, \tfrac{3}{2} \, \frac{\mathbf{R}}{\mathbf{J}} \bigg( \frac{\rho_1}{m_1} + \frac{\rho_2}{m_2} \bigg) \, = \, \tfrac{3}{2} \nu_0 \, \frac{\mathbf{R}}{\mathbf{J}} \, ,$$

and consequently

$$C_v = \frac{5}{2} \frac{R}{Jm_0},$$

By the equation of continuity (12.03), the last equation is equivalent to

(12.14) 
$$\frac{1}{T} \frac{DT}{Dt} - \frac{2}{3} \frac{1}{\nu_0} \frac{D\nu_0}{Dt} = 0,$$

or to

(12.15) 
$$\frac{D}{Dt}(T_{\nu_0}^{-s/s}) = 0 \qquad \frac{D}{Dt}(p_0\nu_0^{-s/s}) = 0.$$

Since we are neglecting diffusion,  $m_0$  (or  $\lambda_1 m_1 + \lambda_2 m_2$ ) is invariable, and (12.15) expresses the adiabatic law of expansion of a monatomic gas as a given element is followed throughout its motion, viz.,

(12.16) 
$$p_0 = k \rho_0^{5/3} \qquad T = k' \rho_0^{2/3}.$$

Thus (12.12) may be regarded as giving the correction to this law owing to diffusion, viscosity, and conduction. The left-hand side represents the net rate of increase of energy of molecular agitation, being the increase corresponding to the rising temperature after allowing for the change of heat energy produced by adiabatic expansion or compression. The right-hand side indicates that this is due to the following causes:—

- (a) We are considering the fluid contained in a volume element which moves with the mean motion of the fluid; but in addition to this motion there is one of interdiffusion within the element, there being a stream of  $\pm (\nu_0 u'_0, \nu_0 v'_0, \nu_0 w'_0)$  molecules per unit time per unit volume in opposite directions. The x-components of the effective forces on each of these molecules are  $X_1 m_1 \frac{Du_0}{Dt}$  and  $X_2 m_2 \frac{Du_0}{Dt}$  respectively, the second term depending on  $\frac{Du_0}{Dt}$  being present, since we are throughout concerned with the energy relative to the mean motion  $(u_0, v_0, w_0)$ . The work done on the fluid by these forces is expressed, in thermal units, by the first right-hand term of (12·12).
- ( $\beta$ ) Owing to the motion of diffusion there will be an increase in the number of molecules  $m_1$  and an equal decrease in the number of molecules  $m_2$ , at the rate of  $\left(\frac{\partial u'_0}{\partial x} + \frac{\partial v'_0}{\partial y} + \frac{\partial v'_0}{\partial z}\right)$  per unit time per unit volume. The mean energy of peculiar motion is the same for molecules  $m_1$  and  $m_2$ , so that this change affects only the energy of mean motion, which is  $\frac{1}{2}m_1c_0^2$  for a molecule  $m_1$ , and  $\frac{1}{2}m_2c_0^2$  for a molecule  $m_2$ . The increase of energy due to this cause is represented by the second right-hand term of (12·12).
- (γ) The third term gives the heat generated by the viscous forces acting in the gas, being, in fact, twice the "dissipation function" of the viscous motion.\*

<sup>\*</sup> Cf. LAMB, 'Hydrodynamics,' p. 518.

- ( $\delta$ ) The fourth term represents the increase of heat which ordinary physics regards as due to conduction, together with a term due to diffusion which has not, so far as I know, been hitherto recognised in either ordinary physics or the kinetic theory. These two terms are discussed in detail in the next section of this chapter.
  - (c) Conduction of Heat and the Thermal Flux of Diffusion.

If there is no mass motion the equation of energy takes the form

(12.17) 
$$\rho_0 C_v \frac{\partial T}{\partial t} = \frac{1}{J} \sum_{\nu_0} u'_0 (X_1 - X_2) - \frac{1}{J} \sum_{\nu_0} \frac{\partial}{\partial x} (\frac{1}{2} \rho_1 \overline{U_1 C_1}^2 + \frac{1}{2} \rho_2 \overline{U_2 C_2}^2),$$

and in the last term we will now substitute from (5.25), with the result

$$(12.18) \quad \rho_{0}C_{v}\frac{\partial T}{\partial t} = \frac{1}{J}\sum \nu_{0}u'_{0}(X_{1} - X_{2})$$

$$+ \frac{1}{9}\sum \frac{\partial}{\partial x}\frac{RT}{J}\left\{A_{0}\xi'_{0}\sum_{1}^{\infty}r\left(\nu_{1}\alpha_{r} + \nu_{2}\alpha_{-r}\right) + B_{0}\frac{\partial T}{\partial x}\sum_{1}^{\infty}\left(\nu_{1}\beta_{r}^{*} + \nu_{2}\beta_{-r}\right)\right\}.$$

It is convenient to eliminate  $\xi'_0$  by means of (3.15), and on so doing (12.18) becomes transformed into

$$(12^{\cdot}19) \quad \rho_{0}C_{v}\frac{\partial T}{\partial t} = \frac{1}{J}\sum_{v_{0}}u'_{0}\left(X_{1}-X_{2}\right)$$

$$+\sum_{v_{0}}\frac{\partial T}{\partial x}\frac{RT}{J}\left[\sum_{v_{1}}^{\infty}r\left(\nu_{1}\alpha_{r}+\nu_{2}\alpha_{-r}\right)u'_{0}+\frac{1}{9}B_{0}\frac{\partial T}{\partial x}\left\{\sum_{v_{1}}^{\infty}\left(\nu_{1}\beta_{r}+\nu_{2}\beta_{-r}\right)\right.\right.$$

$$\left.\left.-\frac{1}{9}\frac{\beta'_{0}}{\alpha'_{0}}\sum_{v_{1}}^{\infty}r\left(\nu_{1}\alpha_{r}+\nu_{2}\alpha_{-r}\right)\right\}\right].$$

If we suppose that no diffusion is taking place, so that  $(u'_0, v'_0, w'_0)$  are all zero, and compare (12.19) with Fourier's equation of conduction of heat in a gas at rest, *i.e.*, with

(12.20) 
$$\rho_0 C_v \frac{\partial T}{\partial t} = \sum \frac{\partial}{\partial x} \left( \Im \frac{\partial T}{\partial x} \right),$$

we obtain the following equation for the coefficient of thermal conduction  $\Im$ :—

$$(12.21) \qquad \qquad \Im = \frac{1}{9} B_0 \frac{RT}{J} \left\{ \sum_{1}^{\infty} \left( \nu_1 \beta_r + \nu_2 \beta_{-r} \right) - \frac{\beta'_0}{\alpha'_0} \sum_{1}^{\infty} r \left( \nu_1 \alpha_r + \nu_2 \alpha_{-r} \right) \right\}.$$

From (12.19) we perceive also that the motion of inter-diffusion is accompanied by a flow of heat, which is proportional to the velocity of diffusion, and also depends on the temperature and the molecular densities, but is independent of the other characteristics of the gas. We shall term this process the thermal flux of diffusion;

in the absence of thermal conduction and of external forces we shall have as the equation of energy

(12.22) 
$$\rho_0 C_v \frac{\partial \mathbf{T}}{\partial t} = \Sigma \frac{\partial}{\partial x} (\mathbf{B} u'_0),$$

where B is defined by the equation

(12.23) 
$$\mathbf{B} \equiv \frac{\mathrm{RT}}{\mathrm{J}} \frac{1}{\alpha'_{0}} \sum_{1}^{\infty} r \left(\nu_{1} \alpha_{r} + \nu_{2} \alpha_{-r}\right),$$

and is termed the specific energy of diffusion.

We now proceed to consider in detail the various coefficients of diffusion, conduction, viscosity, and specific energy of diffusion for which we have obtained general formulæ.

#### § 13. The Coefficient of Diffusion $D_{12}$

#### (a) The General Formula.

The general formula for the coefficient of diffusion  $D_{12}$  is obtainable in terms of the molecular data by substitution in (10.05) of the value of  $\alpha'_0$  given by (5.35), thus

(13.01) 
$$D_{12} = \frac{1}{9} A_0 R T \lambda_1 \lambda_2 \frac{\nabla' (\delta_{mn} a_{mn})}{\nabla (\delta_{mn} a_{mn})}.$$

So far as § 9 (b)  $A_0$  had remained quite arbitrary, only the product of  $A_0$  into the coefficients  $\alpha$  being definite. We there defined  $A_0$  as having such a value as to make  $\alpha_{00}$  equal to unity. We now substitute that value (cf. (9.022)), viz.,

(13.02) 
$$A_0 = \frac{27 (m_1 + m_2)}{2\pi\lambda_1\lambda_2\nu_0 m_1 m_2 K'_{12}(0)}$$

in (13.01), with the result that

(13.03) 
$$D_{12} = \frac{3 (m_1 + m_2) RT}{2 \pi \nu_0 m_1 m_2 K'_{12}(0)} \frac{\nabla' (\delta_{mn} a_{mn})}{\nabla (\delta_{mn} a_{mn})},$$

where  $\nabla'$  is the principal minor of  $\nabla$ .

#### (b) The Case of Maxwellian Molecules.

In the case of Maxwellian molecules it is readily evident from (6.03) that all the elements of the first row and column of  $\nabla (\delta_{mn} a_{mn})$ , save the initial element  $a_{00}$ , are zero. Hence in this case  $\nabla$  is equal to  $a_{00} \nabla'$ , i.e.,

(13.04) 
$$\frac{\nabla'\left(\delta_{mn}\alpha_{mn}\right)}{\nabla\left(\delta_{mn}\alpha_{mn}\right)} = \frac{1}{\alpha_{00}} = 1,$$

$$2 \quad \text{A} \quad 2$$

in view of the convention in § 13 (a) as to the value of  $a_{00}$ . Hence, by (13.03), we have

(13.05) 
$$D_{12} = \frac{3 (m_1 + m_2) RT}{2\pi\nu_0 m_1 m_2 K'_{12}(0)}$$

as the exact value of D<sub>12</sub> when the molecules are Maxwellian. The same result follows readily also from (10.05), (6.03), and (6.04). It is the same, except as regards the notation, as the formula deduced by Maxwell in his second great memoir on the dynamical theory of gases.\*

#### (c) A First Approximation to the Coefficient of Diffusion.

Only in the case just considered does our general formula for  $D_{12}$  reduce to a simple finite form: usually we must, for practical purposes, be content to make approximations to the exact result. As in § 9, this may be effected by taking successive finite convergents to our infinite determinants, which is equivalent to neglecting all terms in the expansion of f(U, V, W) after the first one, two or more at the beginning. Thus for a first approximation, taking only the central element of  $\nabla (\delta_{mn} a_{mn})$ , it is clear that  $\nabla'/\nabla$  is equal to  $1/a_{00}$  or unity simply (cf. § 13a). Hence we have

(13.06) 
$$D_{12} = \frac{3(m_1 + m_2)RT}{2\pi\nu_0 m_1 m_2 K'_{12}(0)}$$
 (1st approximation),

a result which also follows from (10.05) and (9.03). This, it will be noticed, is the same as (13.05), showing that what is in general only a first approximation to  $D_{12}$  is in the case of Maxwellian molecules a strictly accurate result.

The formula (13.06) is not new; it was first given by Langevin,† and subsequently by myself‡ independently. In all these cases, and also in Maxwell's investigation the method used was an approximate one which involves the assumption that the peculiar velocities of the molecules of the two constituent gases are distributed about the separate mean velocities  $c_1$ ,  $c_2$  according to Maxwell's law for the steady state of a gas. The method of the present paper is based on an actual determination of the law of distribution. The assumed law just mentioned, if expressed in the manner adopted in § 3, would involve no  $\alpha$ -coefficient beyond  $\alpha_0$  (neglecting squares or higher powers of the velocity of diffusion  $c'_0$ ). This coincides with the true law only in the case of Maxwellian molecules (§ 6), so that only in that case is (13.06) exact: Maxwell himself did not prove this rigorously, though he obtained the

<sup>\*</sup> MAXWELL, 'Phil. Trans.,' vol. 157 (1866); or 'Scientific Papers,' ii., p. 27.

<sup>†</sup> Langevin, 'Ann. de Chimie et de Physique' (8), v., 245, 1905 : cf. also Enskog, 'Phys. Zeit.,' xii. 533, 1911.

<sup>† &#</sup>x27;Phil. Trans.,' A, vol. 211, p. 499 (35), 1911.

accurate expression. In the general case (13.06) is an approximation only, and the method used by Maxwell and the other writers just named does not afford a ready means of estimating the error involved. The present investigation makes it clear that in extreme cases this is far from small.

## (d) A Second Approximation to the Coefficient of Diffusion.

Passing now to a second approximation, by means of (10.05) and (9.15) we obtain the result

(13.07) 
$$D_{12} = \frac{1}{1 - \epsilon_0} \frac{3 (m_1 + m_2) RT}{2\pi \nu_0 m_1 m_2 K'_{12}(0)}$$
 (2nd approximation).

The correction to (13.06) consists of a factor  $(1-\epsilon_0)^{-1}$ ,  $\epsilon_0$  being given by (9.14) and (9.09)-(9.13); since for Maxwellian molecules  $k_1 = 1$ , it follows from (9.14) that  $\epsilon_0 = 0$  in their case. In order to estimate the importance of  $\epsilon_0$  in other cases we must consider some special typical molecular models, and determine the numerical values of  $\epsilon_0$  for such gases. The most important models are those for which  $K'_{12}(0)$ ,  $k_t$ , etc., are given in § 9 (f).

In paragraph (g) of this section we shall consider in detail the range in the values of  $\epsilon_0$  calculated from these numbers, for various ratios of the molecular masses and diameters. Since  $\epsilon_0$  only affords a second approximation to  $D_{12}$ , however, and not the exact value, it is convenient first of all to examine certain particular cases of our formulæ  $(cf. \S\S 7, 8)$  which throw some light on the accuracy of a second approximation in general.

## (e) The Coefficient of Diffusion when $m_1 : m_2$ and $\sigma_1/\sigma_2$ are Very Large.

In the special case when the mass and size of a molecule of the first kind are so great, compared with that of a molecule of the second kind, that  $m_2/m_1$  is negligible (cf. § 7), we obtain from (10.05), (7.20) and (13.03) the result

(13.08, 9) 
$$D_{12} = \frac{3RT}{2\pi\nu_0 m_2 K'_{12}(0)} \frac{D_0}{D} = \frac{D_0}{D} \frac{3}{16\nu_0 (\sigma_1 + \sigma_2)^2 (h\pi m_2)^{l_2}},$$

where D is a determinant (occupying only a quadrant of the infinite plane) whose general element is given by (7.21), while  $D_0$  is its principal minor. As usual, for Maxwellian molecules  $D_0 = D$ . We proceed to make successive numerical approximations to  $D_0/D$  in the case of molecules of other types.

For molecules which are rigid elastic spheres we have seen (9.32) that

(13.10) 
$$k_t = \frac{(t+2)_t}{(t+\frac{3}{2})_t},$$

so that by (7.21) the general element of D is

(13.11) 
$$\delta_{rs}a_{rs} = \delta_{rs} \frac{(r+s+2)_{r+s}}{(r+\frac{3}{2})_r(s+\frac{3}{2})_s}, \qquad r \geqslant 0, \ s \geqslant 0.$$

The following are the numerical values of the elements as far as the fourth row and column, the exact values being given in the first expression, and the decimal values to three significant figures in the second:—

By neglecting the rows and columns of D after the first, second, third and fourth respectively we obtain the following four successive approximations to D<sub>0</sub>/D:—

TABLE I.

Approximation.	D.	$\mathrm{D}_0/\mathrm{D}.$
Ist	1.000	1.0000
2nd	$\frac{13}{25} = 0.480$	$\frac{13}{12} = 1.0833$ 235
3rd	$\frac{4608}{25.25.49} = 0.150$	$\frac{5100}{4608} = 1.1068$
4th	$\frac{106168100}{5^67^49^2} = 0.035$	$\frac{1185408^4}{1061681} = 1.1165$

The successive approximations to  $D_0/D$  evidently converge with some rapidity to the value 1.12 or, more nearly, 1.13; the correction introduced by the second approximation covers two-thirds of the error of the first.

It is of importance and interest to notice that in this case an exact solution is obtainable by another method, less general than that of this memoir, but more

effective in the particular case before us; this solution is due to LORENTZ, and may be expressed in our notation by\*

(13.13) 
$$D_{12} = \frac{2}{3\nu_0\pi \left(\sigma_1 + \sigma_2\right)^2 \left(h\pi m_2\right)^{1/2}}.$$

This is identical with our own solution (13:09) if

(13.14) 
$$\frac{D_0}{D} = \frac{32}{9\pi} = 1.1317, \dagger$$

and our approximations to  $D_0/D$  show how this numerical value is approached by the successive convergents to our infinite-determinantal solution.<sup>‡</sup> Incidentally, we may notice that (13.14) affords an expression for  $\pi$  of a kind which, so far as I am aware, is quite new.

If the molecules are  $n^{\text{th}}$  power centres of force  $(cf. \S 9 (f))$ , our general formula (13.09) becomes (when  $m_2/m_1$  is negligible)

(13.15) 
$$D_{12} = \frac{D_0}{D} \frac{3\pi}{8\nu_0 I_1(n) \left(h m_1 m_2 K_{12}\right)^{\frac{2}{n-1}} \left(h \pi m_2\right)^{1/2} \Gamma\left(3 - \frac{2}{n-1}\right)},$$

and the general term of the determinant D is given by

(13.16) 
$$\delta_{rs} a_{rs} = \delta_{rs} \frac{\Gamma\left(r+s+3-\frac{2}{n-1}\right)}{(r+\frac{3}{2})_r \left(s+\frac{3}{2}\right)_s \Gamma\left(3-\frac{2}{n-1}\right)}.$$

With this we may compare the exact formula obtained by Jeans (loc. cit.), using the method of Lorentz,

(13.17) 
$$D_{12} = \frac{\frac{2}{3}\Gamma\left(2 + \frac{2}{n-1}\right)}{\nu_0 I_1\left(n\right) \left(h m_1 m_2 K_{12}\right)^{\frac{2}{n-1}} \left(h \pi m_2\right)^{1/2}}.$$

\* Cf. LORENTZ, 'Archives Néerlandaises,' 10, p. 336, 1905; 'Theory of Electrons,' p. 268. Also, for a more general theory along the same lines, cf. Jeans' 'Dynamical Theory of Gases' (2nd ed.), § 333 (654) or § 450 (890).

PIDDUCK, 'Proc. Lond. Math. Soc.' (2), 15, p. 112, 1915, has also deduced Lorentz's result as a special case of the general method of solution by integral equations.

- † [I have now obtained a rigorous proof of this equation and of (13.18).—February 22, 1917.]
- † Cf. the footnote to page 171.

These are equivalent, so that

$$(13.18) \quad \frac{D_0}{D} = \frac{16}{9\pi} \Gamma \left( 2 + \frac{2}{n-1} \right) \Gamma \left( 3 - \frac{2}{n-1} \right) \cdot$$

$$= \frac{16}{9\pi} \left( 1 + \frac{2}{n-1} \right) \frac{2}{n-1} \left( 2 - \frac{2}{n-1} \right) \left( 1 - \frac{2}{n-1} \right) \Gamma \left( \frac{2}{n-1} \right) \Gamma \left( 1 - \frac{2}{n-1} \right)$$

$$= \frac{16}{9} \left( 1 + \frac{2}{n-1} \right) \frac{2}{n-1} \left( 2 - \frac{2}{n-1} \right) \left( 1 - \frac{2}{n-1} \right) \frac{1}{\sin \frac{2\pi}{n-1}},$$

by a well-known formula in the theory of gamma functions. When n = 5 (the case of Maxwellian molecules), the last equation gives  $D_0/D = 1$ , as it should do. When  $n = \infty$ , corresponding to the case of rigid elastic spheres,  $D_0/D = \frac{32}{9\pi}$ , as before. It is of interest to consider one or two intermediate values of n in order to see with what rapidity our determinantal expression for  $D_0/D$  converges to the value given by (13.18); we shall not go beyond a third approximation.

The determinant D, as far as the third row and column, is as follows, where  $\frac{1}{2}m$  has been written in place of  $\frac{2}{n-1}$ :—

(13.19) 
$$D = \begin{bmatrix} 1 & \frac{1-m}{5} & -\frac{1-m^2}{5.7} \\ \frac{1-m}{5} & \frac{13-4m+m^2}{5.5} & \frac{23-27m+5m^2-m^3}{5.5.7} \\ \frac{1-m^2}{5.7} & \frac{23-27m+5m^2-m^3}{5.5.7} & \frac{433-216m+70m^2-8m^3+m^4}{5.5.7.7} \end{bmatrix}$$

In the following table are given the first three approximations to  $D_0/D$  for a few typical values of n, together with the exact values calculated from (13.18):—

TABLE II.

		$\mathrm{D}_0/\mathrm{D}.$					
n.	n. $m.$		Exact value.				
		lst.	2nd.	3rd.	Exact value.		
5 9 13 17 ∞	1 1 2 1 3 1 4 0	1·000 1·000 1·000 1·000	1·000 1·023 1·039 1·049 1·083	1 · 000 1 · 027 1 · 048 1 · 060 1 · 107	1 · 000 1 · 031 1 · 056 1 · 072 1 · 132		

This table well illustrates the general remarks on the convergence\* of our formulæ which were made in  $\S 9 (a)$ .

The next simplest case of a general character which we shall consider is that in which the two sets of molecules are alike in mass and dynamical properties; a special case of this is that of a simple gas, the two sets of molecules being identical—the corresponding coefficient of diffusion  $D_{12}$  will be written  $D_{11}$  and termed the coefficient of self-diffusion. From (10.05), and (8.9), the latter equation being the one appropriate to the case before us, we find that

(13.20) 
$$D_{11} = \frac{3RT}{\pi \nu_0 m K'_{12}(0)} \frac{\nabla'_0}{\nabla_0},$$

where we may now omit the distinguishing suffixes 1, 2;  $\nabla'_0$  is the principal minor of  $\nabla_0$ , whose general element is given by (8.10). We may note that the factor  $\nabla'_0/\nabla_0$  is independent of  $\nu_1$  and  $\nu_2$  (§ 8).

As far as the first two rows and columns,  $\nabla_0$  has the following form:—

(13.21) 
$$\nabla_0 = \begin{vmatrix} 1 & \frac{1}{2}(k_1 - 1) \\ \frac{1}{2}(k_1 - 1) & \frac{1}{20}(11 - 10k_1 + 7k_2) + \frac{2}{25}k_{12}^0 \end{vmatrix}.$$

The first and second approximations to  $\nabla'_0/\nabla_0$  for a few typical molecular models are given in the subjoined table: the model chosen is the  $n^{\text{th}}$  power centre of force, which is equivalent to a rigid elastic sphere when  $n = \infty$ .

Maxwellian Rigid elastic  $\nabla_{\theta}/\nabla$ . n = 17.n = 9. spheres, gas,  $n = \infty$ . n = 5. 1st approximation . 1.000 1.000 1:000 1.000  $\frac{209}{206} = 1.015$ 2nd approximation. 1.0001.004 1.008

TABLE III.

In calculating the approximations to  $\nabla'_0/\nabla_0$  for n=9 and n=17 we have adopted the values 0.420 and 0.390 respectively for  $I_2(n)/I_1(n)$ ; it would be very troublesome

After each step in the approximation the ratio of successive increments seems to become progressively larger, and from Table I. it would be difficult to judge whether  $D_0/D$  converges to 1·12 or 1·13, if we did not know the correct value to be 1·1317.]

<sup>\* [</sup>Added June 2, 1916.—It is interesting to notice that in all the cases in Table II. the error of the third approximation to  $D_0/D$  is equal (to the order of accuracy of one unit in the last figure given) to the difference between the second and third approximations.

to calculate the exact values of these functions, but fortunately the present calculation does not require them to be known with any great accuracy. When n = 5 we have  $I_2(5)/I_1(5) = 0.501$ , and when  $n = \infty$  the value is 0.333 (cf. Jeans' treatise, 2nd ed., § 33), so that the assumed values when n = 9 and n = 7 cannot be materially in error.

The value of  $\nabla'_0/\nabla_0$  is in all the cases considered  $(n=5 \text{ to } n=\infty)$  very nearly equal to unity, the correction introduced by a second approximation being so small that further approximations are not likely to lead to any but a negligible increase in accuracy. Thus the exact value of  $\nabla'_0/\nabla$  in the case of rigid elastic spherical molecules, for instance, is not likely to differ from 1.017 (slightly greater than 1.015) by more than one part in a thousand.

The exact expression for D<sub>11</sub> corresponding to molecules of the type just mentioned is consequently given by the following equation:—

(13.22) 
$$D_{11} = 1.017 \frac{3}{32\nu_0 \sigma^2 (2h\pi m)^{1/2}}$$

(13.23) 
$$= \frac{0.1520}{\nu (2\sigma)^2 (hm)^{1/2}}$$

(13.24) 
$$= 1.200 \frac{\kappa}{\rho},$$

where in the last line we have made use of the formula for the coefficient of viscosity  $\kappa$  for a simple gas, which has already been given by the author ('Phil. Trans.,' A, vol. 216, § 11 (D), p. 337), viz.,

(13.25) 
$$\kappa = 1.016 \frac{5}{64 (2\pi)^{1/2}} \frac{1}{\nu \sigma^2 (hm)^{1/2}}.$$

In my first paper on the kinetic theory ('Phil. Trans.,' A, vol. 211, p. 477, 1912) the formulæ (13.22)-(13.25) were given as above except for the omission of the factors 1.017 and 1.016 in the first and last, which resulted in 0.150 taking the place of 0.1520 in (13.23).

The expression (13.23) for  $D_{11}$  agrees almost exactly also with a result obtained by Piddick\* for the same quantity, by an entirely different method. Mr. Piddick's work is based on Hilbert's transformation of Boltzmann's integral equation for the velocity-distribution function.† His formula for  $D_{11}$  (loc. cit., p. 101, 41) is the same as (13.23) except that the numerical constant, there given only to three places of decimals, is 0.151.

<sup>\*</sup> Pidduck, 'Proc. Lond. Math. Soc.,' (2), 15, p. 89, 1915.

<sup>†</sup> Hilbert, 'Math. Ann.,' 72, p. 562, 1912; Boltzmann, 'Vorlesungen über Gastheorie,' I.

We may also compare (13.24) with the result obtained from the simple mean-free-path theory (first introduced by Maxwell\*) with Jeans' correction† for the persistence of velocities, viz. (in our notation)

(13.26) 
$$D_{11} = 1.34 \frac{\kappa}{\rho}.$$

This is therefore about 10 per cent. larger than the exact value (13.24).

#### (g) The Variation of D<sub>12</sub> with the Relative Concentration of the Component Gases.

In the course of the development of the kinetic theory perhaps no branch has been the subject of more dispute than that dealing with diffusion. The point of greatest difference was the effect on the rate of diffusion of the relative concentration of the diffusing gases. Meyer's elementary mean-free-path theory ‡ led to a formula for  $D_{12}$  according to which the coefficient of diffusion should vary with the proportions of the mixture over the extreme range indicated by the equation

$$\frac{(D_{12})_{\nu_1=0}}{(D_{12})_{\nu_2=0}} = \frac{m_2}{m_1}.$$

Thus, when the molecular masses are very unequal, the range in the value of  $D_{12}$  should be very great. No such large variation is found to exist, however, according to the results of experiment.

MEYER's theory took no account of the tendency of a molecule to persist in motion along its original direction after collision: as Jeans§ has shown in connection with viscosity, however, "persistence of velocities" is a very important fact, the neglect of which leads to grave error in the mean-free-path theory. Kuenen  $\parallel$  has shown that when taken account of in the theory of diffusion, it largely removes the discrepancy between the small observed variations of  $D_{12}$ , and the variations theoretically calculated by the method referred to.

An earlier modification of Meyer's theory by Gross may also be mentioned. This predicts variations of amount similar to those observed, but generally of the wrong sign; its merits are not such as to demand more than this brief historical reference.

- \* Maxwell, 'Scientific Papers,' i., p. 377, or 'Phil. Mag.,' 1860, January-July.
- † JEANS' Dynamical Theory of Gases, p. 273. The whole of the chapter on diffusion (ch. xii. in the second edition) is of great interest, and a general reference may be made to it for comparison both of theory and experiment with the results of this memoir.
  - † MEYER, 'Kinetic Theory of Gases' (English edition), p. 255.
  - § Jeans' 'Dynamical Theory of Gases,' pp. 276, 292.
- | Kuenen, 'Supp. No. 8 to the Communications from the Leyden Physical Laboratory,' January, 1913. Cf. also Jeans' treatise, ch. xiii. (2nd ed.), p. 328.
- ¶ Gross, 'Wied. Ann.,' 40, p. 424, 1890; the disagreement of Gross's theory with experiment has been indicated by Lonius, 'Ann. d. Phys.,' 29, p. 664, 1909.

In sharp distinction from Meyer's theory, Stefan\* and Maxwell† put forward a theory of diffusion which led to the result that D<sub>12</sub> is entirely independent of the ratio  $\nu_1:\nu_2$ , the formula involving only the sum  $\nu_1+\nu_2$  or  $\nu_0$ . Stefan's theory was based on the hypothesis of rigid elastic spherical molecules, and agrees with the corresponding form of our first approximation to  $D_{12}$  (13.06); the same result was subsequently obtained by Langevin<sup>†</sup> and the present author<sup>§</sup> on the most general molecular hypothesis, in the form (13.06). Maxwell's first formula related to the elastic sphere theory, and was greater than that of Stefan by one-third, Maxwell being considerably in error: his second formula related to Maxwellian molecules, and was identical with the exact formula for such molecules given in  $\S 13$  (b). All these results share the property that they are independent of  $\nu_1$ :  $\nu_2$ , and as the present theory shows, all of them are in error in this respect, except Maxwell's second formula. They require to be multiplied by the correcting factor  $\nabla'/\nabla$  of (13.03): this factor is unity in the case of Maxwellian molecules, so that for a mixture of two sets of such molecules  $D_{12}$  is independent of their numerical proportions. This is one of the few properties of a gas which depends in its very nature (i.e., not merely in absolute magnitude) on a particular molecular model: another such property will be noticed in § 14. The fact that the absence of variation is in disagreement with experimental results confirms the conclusion drawn from other sources of evidence that Maxwellian molecules are unsatisfactory representations of actual molecules.

The only other general case of independence of  $D_{12}$  or  $\nu_1 : \nu_1$  is that in which the dynamical properties of the two sets of molecules are alike, as in the case of self-diffusion (§ 13 (f)). Hence we may speak of the coefficient of self-diffusion of a gas without specifying the ratio  $\nu_1 : \nu_2$  in contemplation; in general, on the contrary,  $D_{12}$  is defined only when the value of  $\nu_1 : \nu_2$  is assigned.

In the case when  $m_2/m_1$  is negligible (§ 13 (e)) the mutual encounters of the light molecules are neglected, with the result that in this case also  $D_{12}$  depends only on  $\nu_0$ . This, however, is perhaps hardly to be regarded as an additional exception to the general rule.

The error in the formulæ of STEFAN and the other authors mentioned arose from the neglect of the difference between the actual law of distribution of the peculiar velocities of the molecules and the assumed Maxwellian law. This is taken account of in the present paper, and leads to the correction factor  $\nabla'/\nabla$  in (13.03); we will now proceed to consider how this factor varies with the ratio  $\nu_1 : \nu_2$  by studying the variation of the second approximation to it, i.e.,  $(1-\epsilon_0)^{-1}$ . From this we may readily

<sup>\*</sup> STEFAN, 'Wien. Sitzb.,' 63 (2), p. 63, 1871; 65, p. 323, 1872.

<sup>†</sup> MAXWELL, 'Scientific Papers,' i., p. 392; ii., p. 57 and p. 345. *Cf.* also Boltzmann, 'Wien. Sitzb.,' 66 (2), p. 324, 1872; 78, p. 733, 1878; **86**, p. 63, 1882; 88, p. 835, 1883. Also 'Vorlesungen über Gastheorie,' i., p. 96.

<sup>1</sup> LANGEVIN, loc. cit. ante.

<sup>§ &#</sup>x27;Phil. Trans.,' A, vol. 211, p. 449.

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infer the character of the variation of  $\nabla'/\nabla$  itself, in view of our knowledge of the mode of convergence of the successive approximations as indicated in § 13 (e).

(h) The Variation of 
$$(1-\epsilon_0)^{-1}$$
 with  $\nu_1:\nu_2$ .

So far as regards our detailed discussion of  $\epsilon_0$ , we shall confine ourselves to the case of rigid elastic spherical molecules; for Maxwellian molecules  $\epsilon_0$  is identically zero, while for  $n^{\text{th}}$  power centres of force  $(5 < n < \infty)$   $\epsilon_0$  is intermediate between 0 and the value appropriate to rigid elastic spheres (cf. Tables II., III., § 13), the character of its variations being similar in the two cases.

From  $\S 9$  (c) we have

(13.28) 
$$\epsilon_0 = (k_1 - 1)^2 \frac{b_1 \nu_1^2 + 2b_{12} \nu_1 \nu_2 + b_2 \nu_2^2}{d_1 \nu_1^2 + 2d_{12} \nu_1 \nu_2 + d_2 \nu_2^2},$$

and in the case of rigid elastic spherical molecules  $(cf. \S 9 (c) \text{ and } \S 9 (f))$  we may write

(13.29) 
$$(k_1 - 1)^2 \frac{b_{12}}{d_{12}} = \frac{6 - \frac{5}{3} 6p}{\frac{8}{9} \frac{k}{p} + 78 - \frac{24}{3} 8p},$$

$$(13.30) (k_1-1)^2 \frac{b_1}{d_1} = \frac{{\mu_1}^2}{30 - \frac{1.00}{30} p - 17{\mu_1}^2} (k_1-1)^2 \frac{b_2}{d_2} = \frac{{\mu_2}^2}{30 - \frac{1.00}{30} p - 17{\mu_2}^2},$$

where

(13.31) 
$$p \equiv \mu_1 \mu_2 \qquad k \equiv \left\{ \frac{4\sigma_1 \sigma_2}{(\sigma_1 + \sigma_2)^2} \right\}^2,$$

so that

(13.32) 
$$0 \leqslant p \leqslant \frac{1}{4}$$
  $0 \leqslant k \leqslant 1$ .

Since the suffix 1 refers to the heavier molecules, we have  $\mu_1 \gg \mu_2$  and

$$\frac{b_1}{d_1} \geqslant \frac{b_2}{d_2}.$$

The condition that  $\frac{b_{12}}{d_{12}}$  shall exceed  $\frac{b_2}{d_2}$  is readily proved to be

(13.34) 
$$\frac{\mu_2}{\mu_1} < f(p) \equiv \frac{81 - 342p + 280p^2}{4k + 81p - 180p^2},$$

and it is found that, for the admissible values of p (i.e.,  $0 \le p \le \frac{1}{4}$ ), f(p) is positive and steadily diminishes as p increases; its least value is consequently  $f(\frac{1}{4})$ , which is equal to 13/(9+4k). Since k never exceeds unity,  $f(p) \ge 1$ , and hence  $\mu_{21} \le f(p)$ , so that

$$\frac{b_{12}}{d_{12}} \geqslant \frac{b_2}{d_2}.$$

The sign of equality corresponds to the limiting case k = 1,  $\mu_1 = \mu_2$ , *i.e.*, to the case of self-diffusion, in which instance, therefore,  $b_1/d_1 = b_2/d_2 = b_{12}/d_{12}$ ,  $\epsilon_0$  being independent of  $\nu_1 : \nu_2$ , as we have already seen (§ 13 (f)).

We cannot unconditionally make the further statement that  $b_1/d_1 \gg b_{12}/d_{12}$ , since the necessary condition for this, viz.,  $\mu_1/\mu_2 \gg f(p)$ , is not always fulfilled; but it is easy to prove that

$$\frac{b_1}{d_1} \geqslant \frac{b_{12}}{d_{12}}$$

if

(13.37) 
$$k \gg \frac{1}{4} \frac{\mu_2^3}{\mu_1} (1 + 80\mu_2 - 100\mu_1\mu_2).$$

When  $\mu_1 = \mu_2 = \frac{1}{2}$ , the last condition becomes  $k \ge 1$ , so that if k = 1 we have, as before,  $b_1/d_1 = b_{12}/d_{12}$ ; if  $\mu_1 = \mu_2 = \frac{1}{2}$  and k < 1, then  $b_1/d_1 < b_{12}/d_{12}$ . The condition (13°37) may be roughly expressed by saying that the more equal the molecular masses, the more equal, also, must be the molecular radii in order that  $b_1/d_1$  shall exceed  $b_{12}/d_{12}$ ; or, conversely, the more unequal the masses, the more unequal, also, may be the radii, consistently with the truth of (13°37).

Clearly, if (13.37) is satisfied, and

$$\frac{b_1}{d_1} \gg \frac{b_{12}}{d_{12}} \gg \frac{b_2}{d_2},$$

 $\epsilon_0$  steadily increases as the proportion of the heavier gas varies from 0 to 1, and consequently, also,  $D_{12}$  steadily increases (cf. (13.07)). If, however, (13.37) is not satisfied,  $\epsilon_0$  and  $D_{12}$  will first increase to a maximum and then diminish slightly, as the ratio  $\nu_1 : \nu_0$  increases from 0 to 1.

As regards the actual value of  $\epsilon_0$ , the range (corresponding to all possible ratios of molecular mass or radius) is from the minimum value of  $(k_1-1)^2 c/f$ , which is clearly zero (when  $\mu_2 = 0$  and  $\nu_1 = 0$ , *i.e.*, when the heavier molecules are infinitesimal in number and the lighter molecules are infinitesimal in mass) to the maximum value of  $(k_1-1)^2 b/e$ , which is  $\frac{1}{13}$  (when  $\mu_2 = 0$  and  $\nu_1 \neq 0$ ). The maximum value of  $(k_1-1)^2 a/d$  is  $\frac{3}{209}$ , which lies between the above limits. The corresponding range of  $(1-\epsilon_0)^{-1}$ , the correction factor to the first approximation (13°06) to  $D_{12}$ , which is introduced on making a second approximation, is consequently from 1 to 1°083. Hence, in conjunction with § 13 (e), we may conclude that for rigid elastic spherical molecules the total possible range in the complete correction factor  $\nabla'/\nabla$  to the first approximation to  $D_{12}$  (cf. (13°01)) is from 1 to  $\frac{32}{9\pi}$  or 1°132 (cf. (13°14)).

It would not be difficult to construct a table showing the values of  $(1-\epsilon_0)^{-1}$  for various typical pairs of gases, but owing to the fact that there are three variables concerned (i.e.,  $m_1/m_2$ ,  $\sigma_1/\sigma_2$ , and  $\nu_1/\nu_2$ ) it would need to be somewhat complicated, and

probably little more knowledge would be gained from it than may be deduced from the above discussion and from Table IV. of  $\S 13$  (i).

### (i) Variation of $D_{12}$ with $\nu_1 : \nu_2$ . Comparison with Experiment.

In view of the conflicting theories regarding the relation between  $D_{12}$  and  $\nu_1/\nu_2$ , several series of experiments to test the question were made at Halle during the years 1904–1909, under the direction of Prof. E. Dorn.\* The gases used were helium—argon by Schmidt and Lonius, oxygen—hydrogen by Deutsch and Jackmann, carbon dioxide—hydrogen and oxygen—nitrogen by Jackmann. In Jackmann's summary of the experiments it is pointed out that the observed variations in  $D_{12}$ , though far from negligible, are small compared with those predicted by Meyer's theory, while Gross's theory (cf. § 13 (g)) is equally unsuccessful in that it predicts variations of the right order but in the wrong direction.

JEANS† compares these observations both with MEYER's theory and with the corrected form of MEYER's theory after allowing for the persistence of velocities (cf. § 13 (g)). The following table is taken from § 446 of his treatise (2nd edition), and relates to the pair of gases, helium—argon:—

	D 1	$\mathrm{D}_{12}$ (calculated).			
$ u_1/ u_2.$	D <sub>12</sub> observed (SCHMIDT and LONIUS).	MEYER's theory.	Meyer's theory corrected (Jeans, Kuenen).		
2 · 65 1 · 00	0·961 1·000	0·548 1·000	0·910 1·000		
0.31	1.036	$1 \cdot 526$	1.110		

Table IV.—Variation of D<sub>12</sub> for He-A.

In this table the values of  $D_{12}$  have been multiplied by a factor in order to make the value corresponding to  $\nu_1 = \nu_2$  equal to unity, for convenience of comparison. Jeans remarks, à propos of the above table, that the observed variations of  $D_{12}$  are insignificant compared with those predicted by Meyer's theory, being small even compared with those predicted by the corrected theory, and that Maxwell's simpler formula (according to which  $D_{12}$  is independent of  $\nu_1/\nu_2$ ) is after all the most accurate numerically. We shall see, however, that the present theory, with its correction  $\nabla'/\nabla$  to the usual first approximation (13:06) to  $D_{12}$ , gives results which are in much closer accordance with the observed phenomena.

<sup>\*</sup> SCHMIDT, 'Halle Dissertation' (1904), and 'Ann. d. Phys.,' 14, p. 801, 1904; Deutsch, 'Halle,' 1907; Jackmann, 'Halle,' 1906; Lonius, 'Halle,' 1909, and 'Ann. d. Phys.,' 29, p. 664, 1909, where the results of the whole series of experiments are summarised and discussed.

<sup>†</sup> JEANS' 'Dynamical Theory of Gases' (2nd cd.), § 446.

The following table contains the results of the Halle experiments on  $D_{12}$ , as given in Jackmann's summary. Additional columns give the values of  $(a) \frac{1}{1-\epsilon_0}$ , calculated from (13.28) on the hypothesis that the molecules are rigid elastic spheres\*: (b)  $\nabla'/\nabla$ —cf. (13.01)—estimated from the value of  $\frac{1}{1-\epsilon_0}$  in accordance with § 9 (a) and § 13 (e): and (c) of  $D_{12}$ , obtained by multiplying the values of  $\nabla'/\nabla$  by such a factor as to make the mean of the resulting values of  $D_{12}$  equal to the mean of the corresponding set of observed values. This is all that is here necessary, since we are concerned now only with the variations of  $D_{12}$ , and not with its absolute values.

Table V.—Variation of  $D_{12}$  with  $\nu_1 : \nu_2$ .

Gases. Authority.	$\lambda_1 = \frac{\nu_1}{\nu_1 + \nu_2}.$	$\frac{1}{1-\epsilon_0}$ .	$\frac{ abla'}{ abla'_{\iota}}$ .	$D_{12}$ .		
				Observed.	Calculated.	
Argon-helium.  Schmidt and Lonius, $m_1/m_2 = 10.$	$ \left\{ \begin{array}{l} 0 \cdot 273 \\ 0 \cdot 315 \\ 0 \cdot 377 \dagger \\ 0 \cdot 500 \dagger \\ 0 \cdot 677 \\ 0 \cdot 763 \end{array} \right. $	$1 \cdot 035$ $1 \cdot 040$ $1 \cdot 044$ $1 \cdot 050$ $1 \cdot 058$ $1 \cdot 062$	1·050 1·056 1·063 1·073 1·087 1·094	$0 \cdot 244$ $0 \cdot 250$ $0 \cdot 250^{\dagger}$ $0 \cdot 254^{\dagger}$ $0 \cdot 256$ $0 \cdot 263$	$\begin{array}{c} 0 \cdot 248 \\ 0 \cdot 250 \\ 0 \cdot 251 \\ 0 \cdot 254 \\ 0 \cdot 257 \\ 0 \cdot 259 \end{array}$	
Oxygen-hydrogen.  DEUTSCH $\dagger$ and JACKMANN, $m_1/m_2=16$ .	$ \left\{ \begin{array}{c} 0 \cdot 25 \dagger \\ 0 \cdot 25 \\ 0 \cdot 5 \dagger \\ 0 \cdot 5 \\ 0 \cdot 75 \dagger \end{array} \right. $	$   \left. \begin{array}{c}     1 \cdot 035 \\     1 \cdot 050 \\     1 \cdot 064   \end{array} \right. $	$ \begin{array}{ccc} 1.050 & \{ \\ 1.073 & \{ \\ 1.097 & \end{array} $	0·276† 0·276 0·280† 0·273 0·289†	$ \begin{cases} 0.276 \\ 0.282 \\ 0.289 \end{cases} $	
Carbon dioxide-hydrogen.  DEUTSCH, $m_1/m_2 = 22$ .	$ \begin{cases} 0.25 \\ 0.5 \\ 0.75 \end{cases} $	1·029 1·059 1·070	1·040 1·089 1·108	0.214 $0.218$ $0.228$	$0.212 \\ 0.222 \\ 0.226$	
Nitrogen-hydrogen.  JACKMANN, $m_1/m_2=14$ .	$ \begin{cases} 0.235 \\ 0.5 \end{cases} $	1·030 1·050	1·042 1·073	0·268 0·266	0·263 0·271	
Oxygen-nitrogen.  JACKMANN, $m_1m_2 = 8/7$ .	0.467	1·012 1·013	1·013 1·014	0·0733 0·0730	$0.0731 \\ 0.0732$	

<sup>\*</sup> The values of the molecular radii used in the calculation of  $\epsilon_0$  were taken from the table on p. 476 of my first paper ('Phil. Trans.,' A, vol. 211, 1912); cf. the column there headed "elastic sphere theory."

We may conclude from the above table that the calculated values of  $D_{12}$  are in very satisfactory agreement with the observed data, the differences between the two being not greater than the experimental errors would render probable, if we may judge of these errors from the internal accordance of the observed results. It should also be remembered that the molecular model chosen for calculation is not the best representation of an actual gas molecule, though it is sufficiently good for the purpose, especially in view of its simplicity for numerical work.

#### (j) The Absolute Magnitude of $D_{12}$ .

We next consider the absolute magnitude of the coefficient of diffusion. A comparison of a theoretical expression for  $D_{12}$  with the corresponding observed value involves not only the accuracy of the theory and experiment, but also the suitability of the molecular model adopted as the basis of the theory. If we choose the rigid elastic sphere as model (and for many purposes this very simple model is fairly satisfactory) we may deduce from the observed value of  $D_{12}$  for a specified gasmixture the corresponding value of  $\sigma_1 + \sigma_2$  (cf. (13.01) and (9.31)). By doing this for three pairs of gases A–B, B–C, C–A we can obviously determine from the resulting values of  $\sigma_a + \sigma_b$ ,  $\sigma_b + \sigma_c$ ,  $\sigma_c + \sigma_a$  the individual molecular radii  $\sigma_a$ ,  $\sigma_b$ ,  $\sigma_c$ .\* By taking different sets of pairs we may obtain more than one determination of each molecular radius, and the mutual accordance of these affords some sort of check on the theory—mainly, I think, relating to the suitability of the molecular model. But we cannot in this way test whether the theoretical formula is in error by a factor which is nearly or quite constant, since this would merely alter the deduced values of the radii in a common ratio.

[Revised June 2, 1916.—By another method, as follows, we can to some extent check the absolute magnitude of the theoretical results. Having determined values of  $\sigma$  in the above manner, we can use  $\sigma_1$  (the radius for a particular gas) to calculate  $D_{11}$  by the formula which expresses  $D_{12}$  in the case of dissimilar molecules, putting  $m_2 = m_1$ ,  $\sigma_2 = \sigma_1$ . In this way, practically by interpolation, we obtain a virtually experimental value of  $D_{11}$  (which cannot be measured directly). But the theoretical expression for  $D_{11}$  can also be written in the form  $D'_{11} \equiv k \frac{\kappa_1}{\rho_1}$ ,  $\kappa_1$  and  $\rho_1$  being respectively the viscosity and density of the gas, while k is a numerical constant. If the correct theoretical expression for  $\kappa_1$  is used here, the theoretical value of k should agree with the experimentally measured value  $D_{11}\rho_1/\kappa_1$ . The former depends, of course, on the molecular hypothesis adopted, varying from 1 120 for rigid elastic spheres to 1 504 for Maxwellian molecules. The following table gives several experimental values of k (taken from Jeans' treatise†), which all lie between the

<sup>\*</sup> This method is due to Lord Kelvin, 'Baltimore Lectures,' p. 295.

<sup>†</sup> Cf. Jeans' 'Dynamical Theory of Gases,' 2nd ed., §§ 447, 448. The value of k deduced from the corrected Meyer's theory is  $1\cdot 34$  as against the value  $k=1\cdot 20$  given by the present theory (13·24). The formula for k there used is that given in my second memoir.

values here theoretically deduced. The values of n, calculated from the variation of viscosity with temperature, on the hypothesis that the molecules are the  $n^{\text{th}}$  power centres of force, are given alongside. The formula of interpolation used to obtain  $D_{11}$  from  $D_{12}$  is based on the theory of rigid elastic spherical molecules, and this, together with the rather early date of the diffusion constants used (they were determined by Loschmidt), may prevent us from expecting a very close agreement with theory. I have not calculated the theoretical values of k for values of n between 5 and  $\infty$ , since they depend on certain integrals which must be evaluated by quadratures; but it would be interesting to have these quantities determined.]

					n.	$\frac{\mathrm{D}_{11}\rho_1}{\kappa_1}$ .
Theory					<b>o</b> o	1.200
Hydrogen					12	1.36
Carbon-monoxide.					• 9.3	1.34
Oxygen	٠			.	$7 \cdot 9$	1.43
Carbon-dioxide .					$5\cdot 2$	1.50
Theory					$5 \cdot 0$	1.504

Perhaps the most satisfactory comparison between theory and experiment is provided by calculating  $\sigma_1$  both from the coefficient of diffusion, as above, and also in some other way as, e.g., from the coefficient of viscosity  $\kappa_1$ . Assuming that the experimental data and the molecular representation underlying the theory are satisfactory, the accordance of the two values of  $\sigma$  affords a complete check on the theory of  $D_{12}$  and  $\kappa$  jointly. Such a comparison was made in my first memoir ('Phil. Trans.,' A, vol. 211, p. 480), using the approximate formulæ for  $D_{12}$  and  $\kappa$  there given; the confirmation of the theory thus provided was perhaps as good as the accuracy of the data might allow one to expect. The table in that paper requires revision, because of the corrections to my original formulæ which have been deduced in the present and my second memoir. Until more modern and accurate data for the coefficient of diffusion are available, however (and of such there is need), this revision is hardly worth while in view of the smallness of the corrections mentioned.

In connection with this matter, finally, it may be pointed out that in tables giving values of  $D_{12}$  intended for accurate theoretical purposes it is necessary to specify the ratio by volumes of the diffusing gases, since the theoretical expression for  $D_{12}$ , in general, involves this ratio  $(\nu_1 : \nu_2)$ . This practice has not usually been adopted hitherto.

## (k) The Variation of D<sub>12</sub> with Pressure and Temperature.

Since the theoretical expression for  $D_{12}$ , on whatever molecular hypothesis, contains at least one quantity (molecular diameter or force constant) which is not directly measurable, two or more values of  $D_{12}$ , corresponding to different temperatures or

pressures, are necessary in order to obtain evidence from diffusion as to the best molecular model. It is, therefore, of some importance to consider the variation of  $D_{12}$  with pressure (or density) and temperature.

The first approximation to  $D_{12}$  (13.06) varies as  $T^{\frac{n+3}{2(n-1)}+1}$  in the case of molecules which are  $n^{\text{th}}$  power centres of force, the case  $n = \infty$ ,  $T^{s_{l_2}}$ , corresponding to rigid elastic spheres (cf. 'Phil. Trans.,' A, vol. 211, p. 479). It may readily be seen that the correction factor  $\nabla'/\nabla$  in (13.01) is independent of h or T for these particular molecular models (cf. 'Phil. Trans.,' A, vol. 216, § 9 (B), p. 321).

Another molecular model, considered in my two previous memoirs, is the rigid elastic sphere surrounded by a field of attractive force (the SUTHERLAND molecule). The first approximation to  $D_{12}$  in this varies as  $T^{3/2}/(1+S'/T)$ , where S' is known as SUTHERLAND'S constant of diffusion.\* It may be proved without difficulty, as in the case of the coefficient of viscosity for a simple gas (cf. my second memoir, §§ 9–11) that the correction  $\nabla'/\nabla$  is usually intermediate between unity and the value corresponding to rigid elastic spheres without attraction. The correction factor in the case of SUTHERLAND'S molecules also depends upon the temperature, but the variation is so very slight as to be negligible.

As regards variation with density, the first approximation to  $D_{12}$  varies inversely as the total density of the gas mixture, and is independent of the relative proportions of the two gases. The correction factor  $\nabla'/\nabla$  in (13.01) has been seen to vary with the relative proportions  $(\nu_1/\nu_2)$ , but if  $\nu_1 : \nu_2$  is fixed, the factor may readily be shown not to vary with the total density  $\nu_1 + \nu_2$ .

# § 14. The Coefficient of Thermal Diffusion.

(a) The General Formula for  $D_T$ .

The coefficient of thermal diffusion  $D_T$  was defined in § 10 (a) by the equation

(14.01) 
$$u_0' = -D_{\mathrm{T}} \frac{1}{T} \frac{\partial T}{\partial x} = -D_{\mathrm{T}} \frac{\partial \log T}{\partial x},$$

and was found to be given by (cf. (10·10), (5·36))

$$D_{\mathrm{T}} = -\frac{1}{9} B_0 \beta_0' T = \frac{1}{9} \lambda_1 \lambda_2 B_0 T \frac{\nabla_0' (\delta_{mn} b_{mn})}{\nabla (\delta_{mn} b_{mn})}.$$

In the case of Maxwellian molecules it was found that  $\beta'_0$  vanishes (cf. (6.05)), so that for a gas composed of such molecules  $D_T$  is zero, and the phenomenon of thermal diffusion is non-existent. This, together with the absence of variation of  $D_{12}$  with  $\nu_1/\nu_2$  (cf. § 13 (g)), is one of the few properties of a gas which depends essentially on

<sup>\*</sup> Cf. Sutherland, 'Phil. Mag.' (5), 38, p. 1, 1894, and my first memoir, p. 479.

the particular characteristics of the molecules. We shall see later that the phenomenon is also differential, *i.e.*, it occurs only when the masses or diameters of the molecules are not the same for the two kinds. Thus when they are alike in mass and dynamical properties  $\beta'_0$  (and consequently also  $D_T$ ) is exactly zero (cf. (8.13)); this is true whatever the nature of the molecules.

# (b) The First Approximation to D<sub>T</sub>.

The first approximation to  $D_T$  is obtained by substituting the value of  $\beta'_0$  given, to this degree of accuracy, by (9.20), viz. (cf. (9.17), (9.09)-(9.13)),

(14.03) 
$$D_{T} = \frac{3 (m_{1} + m_{2}) RT}{2\pi\nu_{0} m_{1} m_{2} K'_{12}(0)} \frac{\epsilon_{1} (k_{1} - 1)}{\Delta_{1}\nu_{0}}.$$

We shall not go beyond a first approximation in the general case, but (as in § 13 (e) with regard to  $D_{12}$ ) we shall briefly examine the order of magnitude of the corrections introduced by further approximations, by a consideration of the special case when  $m_2/m_1$  and  $\sigma_2/\sigma_1$  are very small (§ 7).

(c) The Value of  $D_T$  when  $m_1/m_2$  and  $\sigma_1/\sigma_2$  are very large.

In this instance the value of  $\beta'_0$  is given by (7.22), and

(14.04) 
$$D_{T} = \frac{3\lambda_{2}RT}{2\pi\nu_{0}m_{2}K'_{12}(0)}\frac{D'_{1}}{D'}.$$

When the molecules are rigid elastic spheres of radii  $\sigma_1$ ,  $\sigma_2$ , this assumes the form

(14.05) 
$$D_{T} = \frac{3\lambda_{2}}{16\nu_{0} (\sigma_{1} + \sigma_{2})^{2} (h\pi m_{2})^{1/2}} \frac{D'_{1}}{D'},$$

or (cf. (7.26)) the same expression except that  $D_1/D$  replaces  $D'_1/D'$ . In each case the suffix 1 to D or D' denotes the second minor of the corresponding determinant.

We have already given the value of D as far as the fourth row and column (§ 13 (e)). From this we find that the first three approximations to  $D_1/D$  are, with their successive differences equal to

$$\frac{5}{12} = 0.417$$

$$\frac{2280}{4608} = 0.494$$

$$\frac{556416}{1061681} = 0.524.$$

These indicate the magnitude of  $D_1/D$  sufficiently for our purpose, though for an accuracy of (say) I per cent. it might perhaps be necessary to carry the calculation two or three steps further. If we take the limit of these approximations as 0.58, we have (cf. (13.13))

(14.06) 
$$D_{T} = 0.58 \frac{3\lambda_{2}}{16\nu_{0} (\sigma_{1} + \sigma_{2})^{2} (h\pi m_{2})^{1/2}} = 0.51\lambda_{2} D_{12}.$$

In this case, therefore,  $D_T$  is comparable with  $D_{12}$ , though it may be remarked that if  $\lambda_2$  is too nearly equal to unity, our assumption (§ 7) that the effect of collisions among the lighter molecules is negligible may require revision. It may, indeed, be readily seen from the general expression for  $D_T$  that this always vanishes if either  $\lambda_1$  or  $\lambda_2$  becomes zero.

We may briefly examine the case also of  $n^{\text{th}}$  power centres of force by means of (13.19). Considering only a first approximation, the following results are obtained for various values of n:—

First Approximations to D'<sub>1</sub>/D'.

n = 5	(m = 1)	$D'_1/D' = 0$ , exactly.	
n = 7	$(m = \frac{2}{3})$	0°156, app	roximately.
n = 9	$(m = \frac{1}{2})$	0.227	,,
n = 13	$(m = \frac{1}{3})$	0.294	,,
n = 17	$(m = \frac{1}{4})$	0.326	23
n = 33	$(m = \frac{1}{8})$	0.372	,,
$n = \infty$	(m=0)	0.417	,,

The general formula for the first approximation to D'<sub>1</sub>/D' is readily seen to be

$$\frac{5}{2} \frac{1-m}{6-m} = \frac{5}{12} \frac{n-5}{n-\frac{5}{3}} \quad \left(m = \frac{4}{n-1}\right).$$

The last table shows that a very slight excess of n over its value for Maxwellian molecules (n = 5) suffices to raise  $D_T$  to a considerable proportion of its magnitude corresponding to  $n = \infty$  (rigid elastic spheres). The phenomenon of thermal diffusion clearly disappears only under conditions which must be fulfilled with great nicety.

As an instance of the correction introduced by a second approximation in the case of a finite value of n, it may be noticed that the result of a second approximation for n = 9 is 0.246.

# (d) The Approximate Value of $D_T$ when $\sigma_1 = \sigma_2$ and $m_1/m_2$ is very large.

The case considered in the last sub-section is realised physically in a metal or gas, among the molecules of which are found free electrons. Another case of physical importance is that in which the molecules are similar except in mass,  $m_1/m_2$  being large; the diameters of ordinary molecules do not differ greatly, while their masses may be widely different. Thus the diameters of the oxygen and hydrogen molecules are approximately  $1.78 \cdot 10^{-8}$  and  $1.33 \cdot 10^{-8}$  respectively, the ratio of their masses being 16. If in our first approximation to  $D_T$  given by (14.03) we insert the values of  $K'_{12}(0)$ ,  $k_1$ , &c., appropriate to rigid elastic spherical molecules, and write  $\sigma_1 = \sigma_2$ ,  $\mu_1 = 1$ ,  $\mu_2 = 0$ , the result is

$$D_{T} = \frac{15\lambda_{1}\lambda_{2}}{4(9+\lambda_{2})} \frac{3}{16\nu_{0}(\sigma_{1}+\sigma_{2})^{2}} \left(\frac{m_{1}+m_{2}}{hm_{1}m_{2}}\right)^{1/2}, \text{ approximately.}$$

The corresponding value of  $\epsilon_0$  (9.15) is  $3\lambda_1/(39+\lambda_2)$ , so that

$$D_{12} = \frac{39 + \lambda_2}{4(9 + \lambda_2)} \frac{3}{16\nu_0 (\sigma_1 + \sigma_2)^2} \left(\frac{m_1 + m_2}{h m_1 m_2}\right)^{l_2}, \text{ approximately,}$$

and

(14.07) 
$$D_T = \frac{15\lambda_1\lambda_2}{39+\lambda_2}D_{12}, \text{ approximately.}$$

Thus when  $\lambda_1 = \lambda_2 = \frac{1}{2}$ ,  $D_T/D_{12}$  becomes 0.095, which is nearly equal to the maximum value for this particular gas. When  $\lambda_1$  or  $\lambda_2$  vanishes, so also does  $D_T$ , another instance of the general theorem on which remark has already been made.

# (e) General Remarks and Numerical Values.

It is now evident, from the special cases treated in the preceding sub-sections, that the importance of the phenomenon of thermal diffusion, as compared with ordinary diffusion, is greater or less according as the difference between the molecular masses and diameters is large or small. If the mass and diameter of the one set of molecules are very large compared with those for the other set,  $D_T$  rises to about  $\frac{1}{2}D_{12}$ ; if there is a large inequality in mass, but no difference in size,  $D_T$  is about  $\frac{1}{10}D_{12}$  at most\*; if mass and diameter are both the same for the different molecules,  $D_T = 0$ , which is also its limiting value when  $\lambda_1$  or  $\lambda_2$  tends to zero, and its invariable value when the molecules are Maxwellian.

The following are a few values of D<sub>T</sub>/D<sub>12</sub> corresponding to typical pairs of actual

<sup>\*</sup> See Note E (p. 197) for the case of nearly equal masses and very unequal sizes.

gases, and are obtained by comparing the approximations to  $D_T$  and  $D_{12}$  contained in (13.07) and (14.03); calling their ratio  $k_T$ , we have

$$\begin{split} k_{\mathrm{T}} &= \frac{\epsilon_{1} \left( 1 - \epsilon_{0} \right)}{\nu_{0} \Delta_{1}} \\ &= \frac{2 \left( k_{1} - 1 \right) \left[ 15 \left( \lambda_{1} \mu_{2} + \lambda_{2} \mu_{1} \right) \left( \mu_{1} - \mu_{2} \right) - 4 \mu_{1} \mu_{2} k_{12}^{-0} \left( \lambda_{1} - \lambda_{2} \right) + \left( \lambda_{1} \mu_{12} k_{11}^{-0} - \lambda_{2} \mu_{21} k_{22}^{-0} \right) \right]}{d + e^{\frac{\nu_{1}}{\nu_{2}}} + f^{\frac{\nu_{2}}{\nu_{1}}} \\ &= \frac{\frac{2}{3} \mu_{1} \mu_{2} \left( \lambda_{1} - \lambda_{2} \right) + 6 \left( \lambda_{2} \mu_{1}^{2} - \lambda_{1} \mu_{2}^{2} \right) + \left( \lambda_{2} \mu_{1} A_{1} - \lambda_{1} \mu_{2} A_{2} \right)}{A_{1} A_{2} + \left( 6 - \frac{2}{3} \frac{0}{3} \mu_{1} \mu_{2} \right) \left( A_{1} + A_{2} \right) - \frac{1}{5} \left( \mu_{1}^{2} A_{1} + \mu_{2}^{2} A_{2} \right) + \frac{7}{5} \frac{2}{5} - \frac{6}{1} \frac{8}{5} \frac{8}{\mu_{1}} \mu_{1} \mu_{2}}{h_{1} \mu_{2}} \,, \end{split}$$

where

$$A_1 = \frac{4}{3} \frac{\nu_1}{\nu_2 \mu_2} \left( \frac{2\sigma_1}{\sigma_1 + \sigma_2} \right)^2, \qquad A_2 = \frac{4}{3} \frac{\nu_2}{\nu_1 \mu_1} \left( \frac{2\sigma_2}{\sigma_1 + \sigma_2} \right)^2.$$

The values of  $\sigma$  used in calculating the results in the following table are taken from the table on p. 476 of my first memoir.

Table VI.—Comparison of  $D_T$ ,  $D_p$ ,  $D_{12}$ .

	Argon-helium.					gen.	Oxygen-nitrogen.			
		$\frac{m_1}{m_2} = 9.8,$			$\frac{m_1}{m_2} = 16,$		$\frac{m_1}{m_2} = \frac{16}{14}$ ,			
Ratio of the two gaseous com-					$\frac{\sigma_1}{\sigma_2} = 1.34$	,	$\frac{\sigma_1}{\sigma_2} = 0.97,$			
two gaseous components.	wo gaseous components. $k_{\rm T} = \frac{20 \cdot 4\lambda_1 + 4 \cdot 8\lambda_2}{32 \cdot 6 + 58 \cdot 6 \frac{\nu_1}{\nu_2} + 4 \cdot 4 \frac{\nu_2}{\nu_1}}.$			$k_{ ext{T}} = {45}.$	$\frac{28 \cdot 0\lambda_1 + 5}{5 + 78 \cdot 3 \frac{\nu_1}{\nu_2}}$	$\frac{\cdot 2\lambda_2}{+5\cdot 8\frac{\nu_2}{\nu_1}}$	$k_{\rm T} = \frac{0 \cdot 33\lambda_1 + 0 \cdot 41\lambda_2}{22 \cdot 2 + 9 \cdot 3\frac{\nu_1}{\nu_2} + 8 \cdot 7\frac{\nu_2}{\nu_1}}.$			
	$k_{\mathrm{T}} = \frac{\mathrm{D_{T}}}{\mathrm{D_{12}}}, \ k_{p} = \frac{\mathrm{D_{p}}}{\mathrm{D_{12}}}, \qquad \frac{\mathrm{D_{p}}}{\mathrm{D_{T}}}.$		$k_{\mathbf{T}} = \frac{\mathbf{D_{T}}}{\mathbf{D_{12}}}.$	$k_p = \frac{\mathbf{D}_p}{\mathbf{D}_{12}}.$	$\frac{\mathrm{D}_p}{\mathrm{D}_{\mathtt{T}}}$ .	$k_{\mathrm{T}} = \frac{\mathrm{D_{\mathrm{T}}}}{\mathrm{D_{12}}}.$	$k_p = \frac{\mathbf{D}_p}{\mathbf{D}_{12}}.$	$\frac{\mathbf{D}_p}{\mathbf{D}_{\mathtt{T}}}$ .		
$\lambda_1 = \frac{1}{4},  \frac{\nu_1}{\nu_2} = \frac{1}{3}$	0.133	0.513	3.9	0.122	0.592	4.8	0.008	0.026	3.2	
$\lambda_1 = \frac{1}{2},  \frac{\nu_1}{\nu_2} = \frac{1}{1}$	0.132	0 · 408	3.1	0.128	0.441	3.4	0.010	0.033	3.3	
$\lambda_1 = \frac{3}{4},  \frac{\nu_1}{\nu_2} = \frac{3}{1}$	0.079	0.166	2.1	0.079	0.230	2.9	0.007	0.024	3.4	

We may remark, finally, on the direction of thermal diffusion: since D<sub>T</sub> has been found to be a positive quantity (14.01) shows that the heavier gas tends to diffuse towards regions of lower temperature, while the lighter gas tends to diffuse towards those of higher temperature.\*

<sup>\*</sup> Cf., however, Note E, p. 197.

## § 15. The Coefficient of Pressure Diffusion.

In § 10 we saw that, among other causes, a pressure gradient is an agent in producing diffusion, according to the law (cf. (10.08)),

$$(15.01) u_0' = D_p \frac{1}{p_0} \frac{\partial p_0}{\partial x} = D_p \frac{\partial \log p_0}{\partial x},$$

where (cf. (10.09)),

(15.02) 
$$D_{p} = \frac{m'_{0}}{m_{0}} D_{12} = \frac{\lambda_{1} \lambda_{2} (m_{1} - m_{2})}{\lambda_{1} m_{1} + \lambda_{2} m_{2}} D_{12} = k_{p} D_{12},$$

if

(15.03) 
$$k_p \equiv \frac{\lambda_1 \lambda_2 (m_1 - m_2)}{\lambda_1 m_1 + \lambda_2 m_2}.$$

The phenomenon depends essentially on the difference of mass of the molecules, and we may note also that, like thermal diffusion, it tends to zero with  $\lambda_1$  or  $\lambda_2$ . If  $m_1/m_2$  is very large,  $k_p$  clearly has the value  $\lambda_2$ , except when  $\lambda_2$  is very nearly equal to 1.

It is interesting to compare the degree of diffusion produced by equal gradients of  $\log p_0$  and  $\log T$ . This is equivalent to comparing  $k_p$  and  $k_T$ . When  $m_1/m_2$  is very large,  $k_p/k_T = 1/0.51$  or approximately 2, if  $\sigma_1/\sigma_2$  is also large (cf. (14.06)), or  $(39 + \lambda_2)/15\lambda_1$  if  $\sigma_1 = \sigma_2$  (cf. (14.07)), save when  $\lambda_1$  is small. The factor  $k_p$ , unlike  $k_T$ , is not dependent on the relative size of the molecules.

In Table VI. are given the values of  $k_p$  corresponding to the three typical pairs of gases considered in § 14 (c). It appears that  $D_p$  is of thrice or four times the magnitude of  $D_T$  for such gases.

# § 16. The Steady State Without Diffusion.

We will now briefly consider the steady state, without diffusion, of a gas subject to the influence of (a) external forces or (b) boundary conditions which maintain a constant non-uniform distribution of temperature. If we write zero in place of  $u'_0$  in (10.11), and divide by  $D_{12}$ , we have

(16.01) 
$$\frac{\partial \lambda_0'}{\partial x} - 2h \left( X_0' + \frac{1}{\nu_0} \frac{\partial p_0}{\partial x} \right) + k_T \frac{\partial \log T}{\partial x} = 0$$

as the equation of state. It is more convenient to express the middle term as in the following equations (substituting for  $\frac{1}{\nu_0} \frac{\partial p_0}{\partial x}$  from  $2.04 - \frac{\partial u_0}{\partial t}$  being zero, since the state

of the gas is steady—and expressing the result in terms of  $X_1$  and  $X_2$  instead of  $X_0$  and  $X'_0$ ):—

(16.02) 
$$\frac{\partial \lambda_1}{\partial x} = 2h\lambda_1\lambda_2(X_1 - X_2) - k_T \frac{\partial \log T}{\partial x},$$

(16.03) 
$$\frac{\partial \lambda_2}{\partial x} = 2h\lambda_1\lambda_2 (X_2 - X_1) + k_T \frac{\partial \log T}{\partial x}.$$

Since

(16.04) 
$$\frac{\partial}{\partial x} \left( \frac{\nu_1}{\nu_2} \right) = \frac{\partial}{\partial x} \left( \frac{\lambda_1}{\lambda_2} \right) = \frac{1}{\lambda_2} \frac{\partial \lambda_1}{\partial x} - \frac{\lambda_1}{\lambda_2^2} \frac{\partial \lambda_2}{\partial x} = \frac{\lambda_1 + \lambda_2}{\lambda_2^2} \frac{\partial \lambda_1}{\partial x} = \frac{1}{\lambda_2^2} \frac{\partial \lambda_1}{\partial x},$$

we may re-write (16.02) or (16.03) in the form

(16.05) 
$$\frac{\partial}{\partial x} \left( \frac{\nu_1}{\nu_2} \right) = 2h \frac{\nu_1}{\nu_2} (X_1 - X_2) - \frac{1}{\lambda_2^2} k_T \frac{\partial \log T}{\partial x},$$

or

(16.06) 
$$\frac{\partial \log (\nu_1/\nu_2)}{\partial x} = 2h (X_1 - X_2) - \frac{k_T}{\lambda_1 \lambda_2} \frac{\partial \log T}{\partial x}.$$

If the temperature and external forces are uniform, from (16.06) and the two similar y and z equations we may deduce the integral

(16.07) 
$$\frac{\nu_1}{\nu_2} = \left(\frac{\nu_1}{\nu_2}\right)_0 e^{2h} \left\{ (X_1 - X_2)x + (Y_1 - Y_2)y + (Z_1 - Z_2)z \right\},$$

which is a well-known result directly deducible from the statistical theory of distribution of density in a gas.\* If the external forces are gravitational, the z axis being vertically upwards,

$$X = Y = 0,$$
  $Z_1 = -m_1 g,$   $Z_2 = -m_2 g,$ 

and, if g be regarded as constant, we have

$$\frac{\nu_1}{\nu_2} = \left(\frac{\nu_1}{\nu_2}\right)_0 e^{-2hgz(m_1 - m_2)}.$$

The heavier gas, naturally, is relatively denser in the lower strata, the amount of the effect being greater the greater the inequality of mass and the smaller the temperature. In the case of the atmosphere, since the molecular masses of oxygen and nitrogen are nearly equal, the magnitude of this imperfection of diffusion is but small. It is found that the change in the value of  $\nu_1/\nu_2$  would amount only to about  $\frac{1}{5}$  per cent. per kilometre. †

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 $<sup>^{\</sup>star}$  Cf. Jeans' 'Dynamical Theory of Gases' (2nd. ed.), p. 91 (234, 235). † Cf. Jeans' treatise, § 369.

The variation of relative density in the atmosphere due to the temperature gradient (which is about 7° C. per kilometre) is still smaller, and in the opposite direction. Thus, taking  $\nu_1:\nu_2$  for oxygen and nitrogen as 1:3 roughly, and T as 280° C. approximately, the equation giving the variation of  $\nu_1:\nu_2$  near the earth's surface (independently of the effect of the difference in mass) is

$$\frac{\partial}{\partial x} \left( \frac{\nu_1}{\nu_2} \right) = -\frac{1}{\lambda_2^2} k_{\mathrm{T}} \frac{1}{\mathrm{T}} \frac{\partial \mathrm{T}}{\partial x}.$$

By Table VI.,  $k_{\rm T}=0.008$ ,  $\lambda_{\rm 2}=\frac{3}{4}$ , while if we adopt one kilometre as the unit of length, writing T=280 and  $\frac{\partial T}{\partial x}$  as -7, the change in  $\frac{\nu_1}{\nu_2}$  per unit length is found to be

$$\frac{16}{9}$$
. 0.008 ·  $\frac{1}{280}$  · 7 = 0.00035,

or  $\frac{1}{30}$  per cent. per kilometre. This variation is of one-sixth the magnitude of the gravity variation, which it tends to neutralise, since the heavier gas tends to rise owing to the temperature gradient. These changes are masked, however, by the effects of convection currents; it has been found that the proportions of nitrogen and oxygen in our atmosphere are the same for all altitudes up to 10 kilometres, and, indeed, above this height, right into the isothermal layer or stratosphere.

As another instance of the phenomenon of a concentration gradient due to temperature, we may consider the case of a mixture of equal parts (by volume) of oxygen and hydrogen, or argon and helium, placed between two plates which are maintained at freezing and boiling points respectively. Neglecting the small variation in  $\nu_1/\nu_2$ , as far as the integration with respect to x is concerned, in the equation

$$\frac{\partial}{\partial x} \left( \frac{\nu_1}{\nu_2} \right) = -\frac{1}{\lambda_2^2} k_{\mathrm{T}} \frac{\partial \log \mathrm{T}}{\partial x},$$

we may conclude that, independently of the distance between the plates,\* the change in the value of  $\nu_1/\nu_2$  is

$$-4.0^{\circ}130.\log_{e}\frac{373}{273}=0^{\circ}161,$$

where we have taken  $k_{\rm T}=0.130$  (cf. Table VI.), which is approximately the case either for Ar-He or O-H. Thus near the hot plate there will be approximately 48 per cent. of the heavier gas to 52 per cent. of the lighter, and vice versâ near the cool plate. This remarkable result is independent of the pressure of the gas, assuming this to be uniform between the two plates, as will be the case in the

<sup>\*</sup> To the order of accuracy according to which  $k_{\mathrm{T}}$  may be regarded as constant.

absence of external forces; the density, on the other hand, will vary inversely as the temperature.

These numbers are based on the hypothesis that the molecules are rigid elastic spheres; for  $n^{th}$  power centres of force the effect would be somewhat less, vanishing altogether if n = 5. It seems very desirable that the theory should be experimentally tested; the effect predicted is of easily measurable amount, and could be further magnified by taking a greater temperature range. The magnitude of the concentration gradient is so large as to seem improbable, and it is possible that some circumstance has been overlooked which would modify the theory, but I have been unable to detect any such flaw. It is difficult to say how long a time it would take to reach the steady state, or what influence the constant flow of heat through the gas, from the hot plate to the cold, would have upon the phenomenon. (See Note D, p. 196.)

# § 17. The Coefficient of Viscosity.

The general expression for the coefficient of viscosity is (cf. (11.06))

(17.01) 
$$\kappa_{12} = \frac{2}{22.5} \frac{C_0}{2h} \sum_{0}^{\infty} (\nu_1 \gamma_r + \nu_2 \gamma_{-r}).$$

We shall not trouble here to go beyond a first approximation to this expression, even this being somewhat complicated. Referring to (9.27), we obtain the following result as our first approximation:—

(17.02) 
$$\kappa_{12} = \frac{5RT}{\pi K'_{12}(0)} \frac{c_1 \nu_1^2 + 2c_{12} \nu_1 \nu_2 + c_2 \nu_2^2}{k_{11}^0 c_1 \nu_1^2 + 2k_{12}^0 c'_{12} \nu_1 \nu_2 + k_{22}^0 c_2 \nu_2^2}.$$

The values of  $c_1$ ,  $c_2$ ,  $c_{12}$ ,  $c'_{12}$  are defined by (9.28)-(9.30). The equation (17.02) is identical, except as regards notation, with that given in my first memoir on the kinetic theory (*loc. cit.*, p. 451). When  $\nu_2 = 0$ , the formula reduces to

(17.03) 
$$\frac{5RT}{\pi K'_{12}(0)} \frac{1}{k_{11}^{0}} = \frac{5RT}{\pi K_{11}^{2}(0)},$$

which is the first approximation to the coefficient of viscosity of a simple gas composed entirely of molecules of the first kind. Some idea of the accuracy of (17.02) as a first approximation may be gained from the fact that for a simple gas the error (i.e., of (17.03)) amounts to only 1.6 per cent. for rigid elastic spherical molecules, and less for  $n^{\text{th}}$  power centres of force (cf. my second memoir, loc. cit., § 11), the first approximation being too small. How the error varies with  $\nu_1:\nu_2$  cannot be stated without carrying the calculation further, but it is probable that it is always of the same order of magnitude, 1 or 2 per cent. A second approximation to  $\kappa_{12}$  would replace the last factor of (17.02) by the quotient of one homogeneous quartic

polynomial in  $\nu_1$ ,  $\nu_2$  by another, reducing, when  $\nu_2 = 0$ , to the second approximation to  $\kappa_1$ , the coefficient of viscosity of a simple gas. The present importance of such a second approximation to  $\kappa_{12}$  does not seem to render the complicated calculation worth while. In my first memoir (loc. cit., pp. 469-472) a comparison of (17.02) with experimental data is given, which suggests that the formula satisfactorily represents the behaviour of actual gases in respect of the variation of  $\kappa_{12}$  with  $\nu_1/\nu_2$ .\*

When the molecules are rigid elastic spheres, (17.02) has the special form

$$\kappa_{12} = \frac{5}{3^{2}} \left\{ \frac{\text{RT}}{2\pi} \frac{m_{1}m_{2}}{m_{1} + m_{2}} \right\}^{\frac{1}{2}} \frac{\left(1 + \frac{3}{5}\mu_{12}\right)\nu_{1}^{2} + \frac{4}{5}\left\{1 + \frac{3}{2\mu_{1}\mu_{2}} \frac{\sigma_{1}^{2} + \sigma_{2}^{2}}{\left(\sigma_{1} + \sigma_{2}\right)^{2}}\right\}\nu_{1}\nu_{2} + \left(1 + \frac{3}{5}\mu_{21}\right)\nu_{2}^{2}}{\left(1 + \frac{3}{5}\mu_{12}\right)\sigma_{1}^{2}\nu_{1}^{2} + \left\{\frac{1}{2}\left(\sigma_{1} + \sigma_{2}\right)^{2} + \frac{6}{5\mu_{1}\mu_{2}} \frac{\sigma_{1}^{2} + \sigma_{2}^{2}}{\left(\sigma_{1} + \sigma_{2}\right)^{2}}\right\}\nu_{1}\nu_{2} + \left(1 + \frac{3}{5}\mu_{21}\right)\sigma_{2}^{2}\nu_{2}^{2}},$$

where we have quoted from  $\S 9$  (f). The special forms appropriate to molecules of other particular types may likewise easily be written down.

# § 18. The Coefficient of Thermal Conduction.

In § 12 the following expression for the coefficient of thermal conduction  $\Im$  was found (cf. (12.21)):—

$$(18.01) \qquad \qquad \vartheta = \frac{1}{9} B_0 \frac{RT}{J} \left\{ \sum_{1}^{\infty} \left( \nu_1 \beta_r + \nu_2 \beta_{-r} \right) - \frac{\beta'_0}{\alpha'_0} \sum_{1}^{\infty} r \left( \nu_1 \alpha_r + \nu_2 \alpha_{-r} \right) \right\}.$$

Owing to the complexity of even a first approximation, we shall not go further than this in the present paper; in making the approximation, we use the results of § 9, which lead to the equation

$$(18^{\circ}02) \quad \vartheta = \frac{25 \left(\lambda_{1} m_{1} + \lambda_{2} m_{2}\right) \left(m_{1} + m_{2}\right) C_{v} RT}{2\pi m_{1} m_{2} K'_{12}(0) \left(a_{1} \nu_{1}^{2} + 2a_{12} \nu_{1} \nu_{2} + a_{2} \nu_{2}^{2}\right)} \\ \left[\left(\frac{\mu_{2}}{k_{11}^{0}} a_{1} \nu_{1}^{2} + 2a'_{12} \nu_{1} \nu_{2} + \frac{\mu_{1}}{k_{22}^{0}} a_{2} \nu_{2}^{2}\right) - \frac{2}{25} \frac{(k_{1} - 1)^{2} \nu_{1} \nu_{2} \epsilon_{1}^{2}}{d_{1} \nu_{1}^{2} + 2d_{12} \nu_{1} \nu_{2} + d_{2} \nu_{2}^{2}}\right].$$

If we put  $\nu_1 = 0$  in this expression it becomes

(18.03) 
$$\beta = \frac{25 \text{RTC}_{v}}{2\pi k_{11}^{0} \text{K}'_{12}(0)} = \frac{5}{2} \kappa_{1} \text{C}_{v},$$

by (17.03); this agrees with the first approximation to  $\vartheta$  for a simple gas which was given in my two previous memoirs (loc. cit., p. 462, p. 337, respectively). The

\* In particular, the theory there given indicates that the viscosity of a gas mixture may rise to a maximum (for a certain value of  $\nu_1/\nu_2$ ) which exceeds the viscosity of either component separately. This had already been proved by MAXWELL for the particular type of gas dealt with in his second paper. KUENEN has recently shown that the ordinary elastic-sphere theory leads to a similar result, when allowance is made for the persistence of velocities after collision ('Amsterdam Acad. Proc.,' 16, p. 1162, 1914).

expression in (1802) for a composite gas does not, however, agree with the corresponding first approximation in my original memoir ('Phil. Trans.,' A, vol. 211, p. 452, cf. 40 and 41). This is because it was there assumed (§ 2) that thermal conduction was independent of diffusion, whereas we have seen that a temperature gradient is inseparable from either diffusion or a concentration gradient; this invalidates the equations (24) of that paper. The second term within the square bracket of (1802) especially arises from the terms in the velocity-distribution function which represent the diffusion effect, although the first term is also affected. Evidently even the first approximation to  $\Im$  involves the quotient of a homogeneous quartic in  $\nu_1$ ,  $\nu_2$  by the product of two homogeneous quadratics, a complexity which makes it hardly worth while to compare the result with the scanty experimental data at present available. A brief discussion of my earlier formula, which may be expected to differ only slightly from (1802) in numerical magnitude, is given in §18 of my first memoir.

# § 19. The Specific Energy of Diffusion.

In § 12 (c) we saw that in a gas which is at rest and at a uniform temperature, so that no conduction of heat is taking place, there may yet be a continual rise in temperature if diffusion is going on. The gas being at rest as a whole, no gain of thermal energy accrues through the medium of internal friction, and the thermal flux of diffusion may proceed also in the absence of external forces, i.e., solely as a result of variations of concentration. However the diffusion is produced, in the latter or any of the other ways described in § 10, the equation of energy will contain a term equivalent to that on the right of the following equation:—

(19.01) 
$$\rho_{0}C_{v}\frac{\partial T}{\partial t} = \sum \frac{\partial}{\partial x}(\mathbf{B}u'_{0}).$$

This is identical with (12.22), and assumes that only the thermal flux of diffusion is operating to increase the heat energy of the gas.

By (12.23) we have the following expression for  $\blacksquare$ , which we have termed the specific energy of diffusion:—

(19.02)
$$\mathbf{B} = \frac{RT}{J} \frac{1}{\alpha'_{0}} \sum_{1}^{\infty} r \left(\nu_{1}\alpha_{r} + \nu_{2}\alpha_{-r}\right)$$

$$= -\frac{RT}{J} \frac{B_{0}\beta'_{0}}{A_{0}R\alpha'_{0}} \frac{\nu_{0}}{\lambda_{1}\lambda_{2}}$$

$$= -\frac{\nu_{0}}{\lambda_{1}\lambda_{2}} \frac{RT}{J} \frac{D_{T}}{D_{12}},$$

by (9.20) and (10.05), (10.10). Since  $C_v$ , the specific heat at constant volume for the composite gas, is given by

(19.03) 
$$C_v = \frac{3}{2} \frac{R}{Jm_0}$$

we have, writing  $k_{\rm T}$  for  $D_{\rm T}/D_{12}$ , as in § 14,

(19.04) 
$$\mathbf{D} = -\frac{2}{3} \frac{\nu_0 m_0 C_v T}{\lambda_1 \lambda_2} k_T$$
$$= -\frac{2}{3} \frac{k_T}{\lambda_1 \lambda_2} \rho_0 C_v T.$$

Thus we may write (19.01) in the form

(19.05) 
$$\rho_0 C_v \frac{\partial T}{\partial t} = -\sum_{\tau} \frac{\partial}{\partial x} \left\{ \frac{2}{3} \frac{k_T}{\lambda_1 \lambda_2} \rho_0 C_v T u_0' \right\}.$$

We may notice that there is an interesting analogy between this equation and the ordinary equation of continuity

(19.06) 
$$\frac{\partial \rho_0}{\partial t} = -\sum \frac{\partial}{\partial x} (\rho_0 u_0),$$

which refers the rate of concentration of matter in a volume element to the differential rate of transfer of matter across its extent. In the case of diffusion, the opposing inter-diffusing streams carry equal numbers of molecules in opposite directions, but while the energy of molecular agitation is the same for either group of molecules, the kinetic energy of diffusion is different, owing to the different masses with the same velocity of diffusion  $\pm (u'_0, v'_0, w'_0)$ . It is, I imagine, to this cause that the thermal flux of diffusion is due, though the suggestion is only tentative and does not affect the accuracy of (19.05) one way or the other. It is clear, however, that if the velocity of diffusion is such as to cause a concentration of the more massive molecules in any region, at the expense of the lighter molecules (since the total number  $\nu_0$  is not affected by diffusion), the temperature of the region will rise,  $k_{\rm T}$  being positive (§ 14); this readily follows from a comparison of (19.05) and (19.06). From our discussion of the magnitude of  $k_{\rm T}$  in § 14, it appears that the specific energy of diffusion is greater the greater the difference in mass and size between the molecules, as we should expect.

# § 20. Appendix on the Inequality of Temperature between the Component Gases.

Up to the end of § 3 the equations of this paper take account of the possibility of a difference of temperature (as defined in § 1 (c)) between the component gases. After that point it is virtually assumed that  $T'_0$  is zero. We will now briefly consider what modification must be made in order to cover the general case.

It is clear from (3.151) that the component gases have different temperatures only when the ratio of the two gases, by volume, is changing with time. Consequently in

all steady states the temperatures are the same, although the gas may be non-uniform in temperature, velocity, or composition; in this case §§ 4–19 give a complete account of the first-order phenomena of the gas.

When the relative proportions of the component gas are varying, so that the temperatures are unequal, the determination of the coefficients  $\alpha$ ,  $\beta$ ,  $\gamma$  in §§ 4–9 is unaffected, but we must examine how far the physical equations of the succeeding sections remain valid. It is immediately evident that all the phenomena grouped under the general term "diffusion" (cf. § 10 and §§ 13–16) are uninfluenced by the presence or absence of the temperature difference, because the former depend solely on the terms in  $f/(f)_0$  which are of odd degree in U, V, W (cf. § 3 ( $\alpha$ )), while the terms relating to  $T'_0$  or  $\frac{\partial \lambda'_0}{\partial t}$  are of even degree.

Further, it is readily manifest that the equations of viscosity are likewise unmodified. The mean hydrostatic pressures of the component gases  $p_1$ ,  $p_2$  are indeed altered, but their sum  $p_0$  remains constant with the value defined in terms of  $\nu_0$  and  $T_0$  by (1.18). Since the series  $J(C^2)$  of § 3 (a) is symmetrical in  $\cup$ ,  $\vee$ ,  $\vee$ , the partial pressures  $(p_{xx})_1, (p_{yy})_1, (p_{zz})_1$  are all affected equally with  $p_1$ , and similarly for the corresponding pressures for the second component gas. The differences  $p_{xx}-p_0$ ,  $p_{yy}-p_0$ ,  $p_{zz}-p_0$  are therefore independent of  $T'_0$ , and it is clear from (3.03), (3.04) that this is true also of  $p_{yz}$ ,  $p_{zx}$ ,  $p_{zy}$ . Hence the equations of viscous stress given in § 11 are applicable both to steady and unsteady states of the gas.

Finally, it may be seen on inspection that the equation of energy, deduced in § 12, is true independently of the existence of a temperature difference between the component gases. The equations (12.06), (12.07), on which the equation of energy is based, remain true in all cases, if T is taken to be  $T_0$ . Also the presence of the even power series  $J(C^2)$  in the expression for f(U, V, W) does not affect the value of  $\overline{UC^2}$ , so that the expressions of § 12 (c) for the coefficient of thermal conduction and the specific energy of diffusion are universally true.

It remains only to form an estimate of the magnitude of  $T_0$  by determining approximately the coefficients  $\delta_r$  in  $J(C^2)$ . For this purpose it is simplest to make use of equation (2.23), viz.,

(20.01) 
$$\frac{(2h_0m_1)^s}{1 \cdot 3 \cdot 5 \dots (2s+1)} \Delta C_1^{2s} = \nu_0 \frac{\partial \lambda'_0}{\partial t} = -\frac{(2h_0m_2)^s}{1 \cdot 3 \cdot 5 \dots (2s+1)} \Delta C_2^{2s}.$$

Then it may readily be proved, after the manner of §§ 6, 7 of my second paper (loc. cit.), and as a consequence of the expressions (3.03), (3.04) for f(U, V, W), that

$$(20.02) \frac{(2h_0m_1)^s}{1.3.5...(2s+1)} \Delta C_1^{2s} = 32D_0 \frac{\partial \lambda'_0}{\partial t} \sum_{r=0}^{\infty} \left[ \{ d_{1111}(r,s) + d_{1212}(r,s) \} \delta_r + d_{2112}(r,s) \delta_{-r} \right],$$

$$(20^{\circ}03) \frac{(2h_0m_3)^s}{1 \cdot 3 \cdot 5 \dots (2s+1)} \Delta C_2^{2s} = 32D_0 \frac{\partial \lambda'_0}{\partial t} \sum_{r=0}^{\infty} [d_{1221}(r,s) \delta_r + \{d_{2222}(r,s) + d_{2121}(r,s)\} \delta_{-r}],$$

where

$$(20.04) d_{1111}(r, s) = N_{r-1, s-1} \nu_1^2 \iint e^{-(x^2+y^2)} x^2 y^2 \sum_{k=0}^{r, s} \phi_{11}^{k}(y) B_{1111}^{k}(r, s) dx dy,$$

$$(20.05) d_{1212}(r, s) = N_{r-1, s-1} \nu_1 \nu_2 \iint e^{-(x^2+y^2)} x^2 y^2 \sum_{k=0}^{r, s} \phi_{12}^k(y) B^k_{1212}(r, s) dx dy,$$

$$(20.06) d_{2112}(r, s) = N_{r-1, s-1} \nu_1 \nu_2 \iint e^{-(x^2+y^2)} x^2 y^2 \sum_{k=0}^{r, s} (-1)^k \phi_{12}^{k}(y) B_{2112}^{k}(r, s) dx dy.$$

There are similar equations in which the suffixes 1, 2 are interchanged, which need not be written down.

From a comparison of (20.01) with (20.02), (20.03) we obtain the following equations for  $\delta_r$ ,  $\delta_{-r}$ :—

$$(20.07) 32D_0 \frac{1}{\nu_0} \sum_{0}^{\infty} \left[ \left\{ d_{1111}(r,s) + d_{1212}(r,s) \right\} \delta_r + d_{2112}(r,s) \delta_{-r} \right] = 1,$$

$$(20.08) 32D_0 \frac{1}{\nu_0} \sum_{0}^{\infty} \left[ d_{1221}(r, s) \delta_r + \left\{ d_{2222}(r, s) + d_{2121}(r, s) \right\} \delta_{-r} \right] = -1.$$

In these equations s ranges from 1 to  $\infty$  (that the zero value is excluded may be readily seen from § 2 (c), (e)). Similarly r effectively ranges over the same values, since it is clear from (20°04)–(20°06) that d(0, s) = 0 in all cases.\* Hence the equations (20°07), (20°08) do not enable us to determine  $\delta_0$  and  $\delta_{-0}$ , which are given by (3°101), (3°102) in terms of the remaining  $\delta$ 's. Indeed, to obtain  $T_0$  in terms of  $\frac{\partial \lambda_0'}{\partial t}$ , by means of (3°151), we need only to calculate  $\sum_{1}^{\infty} r \delta_r$  or  $\sum_{1}^{\infty} r \delta_{-r}$  (cf. (3°122)).

Symmetrical determinantal expressions for these can be deduced as in § 5, if desired, but we shall be content here to determine  $\delta'_0$  to a first approximation only.

The two central terms of the two central equations of type (20°07), (20°08) are

$$(20.09) 32D_{0} \frac{1}{\nu_{0}} [\{d_{1111}(1, 1) + d_{1212}(1, 1)\} \delta_{1} + d_{2112}(1, 1) \delta_{-1}] = 1,$$

(20.10) 
$$32 D_0 \frac{1}{\nu_0} d_{1221}(1, 1) \delta_1 + \{\partial_{2222}(1, 1) + d_{2121}(1, 1)\} \delta_{-1} = -1,$$

and it may readily be seen that

(20.11) 
$$d_{1111}(1, 1) = \frac{\pi}{144} \nu_1^2 K'_{11}(0),$$

(20.12) 
$$d_{2222}(1, 1) = \frac{\pi}{144} \nu_2^2 K'_{22}(0),$$

$$(20.13) \quad d_{1212}(1, 1) = -d_{1221}(1, 1) = d_{2121}(1, 1) = -d_{2112}(1, 1) = -d_{2112}(1, 1) = \frac{\pi}{36} \,\mu_1 \mu_2 \nu_1 \nu_2 K'_{12}(0).$$

\* When r or s is zero, k = 0, and  $\phi^k(y) = 0$ . Cf. (4.17).

Hence, if we assign to D<sub>0</sub> (which has so far been arbitrary) the value given by

(20.14) 
$$D_0 = \frac{9\nu_0}{8\pi\mu_1\mu_2\nu_1\nu_2K'_{12}(0)},$$

we may write the equations (20.09), (20.10) as follows:—

(20.15) 
$$\left(1 + \frac{\lambda_{12}k_1^0}{4\mu_1\mu_2}\right)\delta_1 - \delta_{-1} = 1,$$

$$(20.16) -\delta_1 + \left(1 + \frac{\lambda_{21}k_2^0}{4\mu_1\mu_{2}}\right)\delta_{-1} = -1.$$

We have here introduced the notation

(20.17) 
$$k_{1}^{0} \equiv \frac{K'_{11}(0)}{K'_{12}(0)}, \qquad k_{2}^{0} \equiv \frac{K'_{22}(0)}{K'_{13}(0)}.$$

From (3.122) we deduce the following equation for  $\delta'_0$ :—

(20.18) 
$$\delta'_{0} = -2\lambda_{1}\lambda_{2} \sum_{r=1}^{\infty} r \left(\delta_{r} - \delta_{-r}\right).$$

The first approximation to this is found, from (20.15), (20.16), to be given by

(20.19) 
$$\delta'_{0} = -2\lambda_{1}\lambda_{2} \frac{\lambda_{12}k_{1}^{0} + \lambda_{21}k_{2}^{0}}{\lambda_{12}k_{1}^{0} + \lambda_{21}k_{2}^{0} + \frac{k_{1}^{0}k_{2}^{0}}{4\mu_{1}\mu_{2}}}.$$

Hence, by (3.151) and (20.14) we have

$$(20^{\circ}20) \qquad T'_{0} = \frac{1}{3}D_{0}^{\circ}T_{0}\delta'_{0}\frac{\partial\lambda'_{0}}{\partial t}$$

$$= -\frac{3T_{0}}{4\pi\nu_{0}\mu_{1}\mu_{2}K'_{12}(0)}\left\{1 + \frac{k_{1}^{\circ}k_{2}^{\circ}}{4\mu_{1}\mu_{2}\left(\lambda_{12}k_{1}^{\circ} + \lambda_{21}k_{2}^{\circ}\right)}\right\}^{-1}\frac{\partial\lambda'_{0}}{\partial t}$$

$$= -\frac{1}{3}D_{12}^{\circ}\frac{m_{1} + m_{2}}{2R}\left\{1 + \frac{k_{1}^{\circ}k_{2}^{\circ}}{4\mu_{1}\mu_{2}\left(\lambda_{12}k_{1}^{\circ} + \lambda_{21}k_{2}^{\circ}\right)}\right\}^{-1}\frac{\partial\lambda'_{0}}{\partial t}$$

$$\equiv -I_{\lambda}\frac{\partial\lambda'_{0}}{\partial t},$$

where  $D_{12}^{0}$  is the first approximation to the coefficient of diffusion (cf. (13.08)), while  $I_{\lambda}$  is a new quantity, defined by the last equation, which we may term the anisothermal diffusion constant.

We may easily gain some idea of the order of magnitude of  $I_{\lambda}$  if we consider two gases of similar dynamical properties, *i.e.*, such that  $m_1 = m_2$ , and  $k_1^0 = k_2^0 = 1$ . The VOL. CCXVII.—A.

last factor in  $I_{\lambda}$  is nearly equal to unity, so that we shall neglect it in our approximate calculations. In this case, therefore,

$$I_{\lambda} = -\frac{1}{3} \frac{D_{11}^{0}}{R/m}.$$

For oxygen the value of  $D_n^0$  is approximately 0.19 (cf. Jeans' treatise, p. 335), while  $R/m = 260 \cdot 10^4$  (loc. cit., p. 131). Hence  $I_{\lambda} = 0.24 \cdot 10^{-7}$  approximately. Thus if the density-ratio of the two gases is changing by 1 per cent. per second, the difference of temperature, if they are equally mixed (i.e.,  $\lambda_1 = \lambda_2 = \frac{1}{2}$ ), is approximately one thousand-millionth of a degree centigrade.\* The hotter gas is the one which is diminishing in relative concentration. In fact, we may perhaps regard the slightly excess speed of the molecules of this gas as the cause of its relative expansion and consequent rarefaction. It is clear from these figures, however, that the phenomenon is likely to be of very minute dimensions in ordinary cases.

\* Thus  $T'_0 = \lambda_1 \lambda_2 (T_1 - T_2) = \frac{1}{4} (T_1 - T_2) = -0.24.10^{-7} \frac{\delta \lambda_0}{\delta t} = -0.24.10^{-9}$ , so that  $T_1 - T_2 = -10^{-9}$  approximately.

[Since this paper was communicated to the Royal Society, this part of the theory has been experimentally tested and confirmed, at least qualitatively. An account of the preliminary qualitative experiments, made by Dr. F. W. Dootson, will be found in the 'Philosophical Magazine,' xxxiii, p. 248.—Note added February 22, 1917.]

[Recently I have succeeded in proving the identity of  $\pi$  and  $\sin \pi x$  with the determinants referred to, using elementary algebraical methods. The construction of a formal justification of the analytical methods used in the present paper is also being proceeded with, and I hope to be able later to deal with the questions of convergence raised here, and to bring the present theory into satisfactory relation with that based on Boltzmann's equation.—Note added February 22, 1917.]

[In a later paper it will be shown that considerations of convergence require a re-grouping of the terms in these expansions, so that they become series of polynomials in C<sup>2</sup>. The expansions are really used in this form in the present paper, the re-grouping of the terms being effected by means of the difference-transformations described in § 5 (d).—Note added February 22, 1917.]

[Since the above was written the indicated result has been qualitatively confirmed in the case of three pairs of gases. The time taken to attain the steady state was only a few hours in the experiments referred to; they are described in a Note by Dr. F. W. Dootson and the author in the 'Philosophical Magazine,' xxxiii, p. 248.—Note added February 22, 1917.]

Note E. (To pp. 158, 184, 185.)

[In a note recently communicated to the 'Philosophical Magazine,' I have considered thermal diffusion in the case of two molecules nearly or quite equal in mass, and very unequal in size. If the difference of mass is sufficiently small, the larger molecules will tend towards the cooler regions.—April 30, 1917.]

Note F. (To p. 115.)

[In his 'Inaugural Dissertation,' Upsala, 1917 (received just before the final revision of the proofs of this paper), D. Enskog gives a mathematical theory of simple and composite monatomic gases, based upon Boltzmann's integral equation for the velocity-distribution function. The method of solution is, however, different from that of his 1912 paper. The numerical and other results, including those relating to thermal diffusion, are in agreement with those of this paper, though not always identical in form. While perhaps less developed from the physical standpoint, Dr. Enskog's work is mathematically much the more complete. His elegant and accurate proofs will materially lighten the task of proving my own work to be in conformity with Boltzmann's equation.—April 30, 1917.]

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REPORT TO THE GOVERNMENT OF CEYLON

ON THE

# PEARL OYSTER FISHERIES OF THE GULF OF MANAAR. By W. A. HERDMAN, D.Sc., F.R.S.

(With Supplementary Reports upon the Marine Biology of Ceylon by various Naturalists.)

Parts I.-V., 1903-1906.

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# VI. Monoclinic Double Selenates of the Nickel Group.

By A. E. H. TUTTON, D.Sc., M.A., F.R.S.

Received and Read November 23, 1916.

This communication deals with the four double selenates of the series  $R_2M(SeO_4)_2$ .  $6H_2O$ , in which M is nickel and R is potassium, rubidium, caesium, and ammonium. Potassium nickel selenate and ammonium nickel selenate only have been previously investigated, and to a very limited extent, by vom Rath and Topsøe and Christiansen; rubidium nickel selenate and caesium nickel selenate do not appear to have formed the subject of either goniometrical or physical investigation.

Great care has been taken with the preparation of the four double salts in a state of The solutions in pure water from which the crystals were deposited contained in each case the two simple constituent salts in exactly equal molecular proportions. Good crystallised specimens of potassium selenate and ammonium selenate were already in the author's possession, and the selenates of cæsium and rubidium were prepared by dissolving the pure carbonates of the two metals in the exact quantity of pure selenic acid, all trace of carbonic acid being removed by boiling. The nickel selenate was prepared in the four cases separately, by dissolving in pure water the quantity of nickel sulphate corresponding molecularly to the amount of the alkali selenate to be used in the preparation of the double salt, and adding a very slight excess of caustic potash solution (freshly prepared from the weighed quantity of solid potash) in order to precipitate all the nickel as nickelous hydrate. After warming, so as to complete the precipitation, the liquid was allowed to stand until the precipitate had settled, when it was washed with a large volume of water, six times by decantation and six further times on the filter. The nickelous hydrate was then dissolved in the calculated amount of selenic acid, the filtered solution of nickel selenate was added to the alkali selenate solution, and the whole allowed to crystallise in successive crops by spontaneous evaporation, with all the precautions indicated on p. 9 of the author's 'Crystallography and Practical Crystal Measurement.'

Potassium Nickel Selenate  $K_2Ni(SeO_4)_2$ .  $6H_2O$ .

Morphology.

Some crystals of this salt were measured in the year 1862 by VOM RATH.\* They were of a very simple character, comprising only four forms, and it is somewhat

'Pogg. Ann. der Phys.' (1862), vol. 115, p. 484, and vol. 116, p. 363.

singular that even in the very numerous (over 30) crops prepared in the course of the work now described no other than these same four forms have been observed on this member of the great monoclinic series.

The crystals are bright green in colour.

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

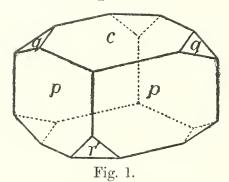
Ratios of Axes.—

a:b:c=0.7467:1:0.5059. Values of vom Rath, 0.7453:1:0.5060.

Axial Angle.— $\beta = 104^{\circ} 27'$ . Value of vom RATH,  $104^{\circ} 53'$ .

Forms Observed.—c {001}, p {110}, q {011}, and r' { $\overline{2}$ 01}.

Habit.—Tabular parallel to c {001}, to short prismatic parallel to p {110}. A common intermediate type is shown in fig. 1.



Eleven small crystals were measured, selected from four different crops. Greater difficulty than usual was experienced in obtaining crystals free from serious striation of the  $p\{110\}$  and  $c\{001\}$  faces, and a very large number of crops were grown, from two entirely distinct preparations, before satisfactory small crystals were produced. The striation affects the values of the angles pp and cp particularly, rendering pp(=2ap) considerably too large, pp (=2bp) conversely too small to the same extent (possibly as much as five minutes), and cp to a less degree (2' or 3') too large. fact was established by measuring a number of crystals affected by the striation and comparing the results with those derived from the perfect crystals used in the measurements recorded in the table, which represent the true value of the angles. The unusual prevalence of such striation of the p and c faces is also responsible for the more than usual discrepancy between the observed and calculated values of the angle cr', in cases like that of the salt under consideration, in which the r' faces were perfect (yielding brilliant single images of the signal) and in which the c faces, when adjusted for the measurement of this orthozone, gave also indubitably placed images, all the images of the bundle coalescing for this zone in the same vertical line.

The faces of q {011} were usually relatively much smaller than those of the basal pinakoid c {001}, as shown in fig. 1, and the faces of r'{ $\bar{2}$ 01} were usually also small, although generally somewhat larger than the q faces. Occasionally, in particular crops, the q faces were relatively larger and the c faces correspondingly less.

Of the only four forms observed,  $c\{001\}$  and  $p\{110\}$  thus usually largely predominate and determine the habit.

# Interfacial Angles of Potassium Nickel Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calcu- lated.	Diff.	Values of vom Rath.
$\begin{cases} ac &= (100): (001) \\ as &= (100): (101) \\ sc &= (101): (001) \\ cr' &= (001): (201) \\ cs' &= (001): (101) \\ s'r' &= (101): (201) \\ r'a &= (201): (100) \\ r'c &= (201): (001) \\ \end{cases} \\ \begin{cases} ap &= (100): (110) \\ pp' &= (110): (120) \\ p'b &= (120): (010) \\ pp'''' &= (110): (130) \\ pp''''b &= (130): (010) \\ pp &= (110): (110) \\ pp &= (110): (110) \\ \end{cases} \\ \begin{cases} cq &= (001): (011) \\ qb &= (011): (010) \\ qq &= (011): (011) \\ qq &= (011): (110) \\ qq &= (011): (111) \\ qq &= (110): (101) \\ qq &= (110): (110) \\ qq &= (110): (111) \\ qq &= (110): (111)$	38 38 38 38	63 20- 63 28	63 24  63 24  116 36  71 48 108 12 26 6  127 48  78 20 85 35 94 25 116 5 52 22 127 39	75 33 46 15 29 18 63 13 38 16 24 57 41 14 116 47 35 54 19 28 34 38 29 22 24 44 54 6 63 54 * 49 30 27 33 77 3 34 26 68 31 35 0 43 20 * 49 30 27 33 77 7 44 33 101 40 53 50 46 69 56 20 4 65 10 24 50 38 27 85 37 55 56 94 23 45 10 26 52 37 36 36 55 70 55 116 5 34 38 92 54 52 28 127 32	11	75 7 — 63 35 — 63 35 — — 71 32 — 71 32 — 77 58 — — — — — — — — — — — — — — — — — — —
measurements	. 414					

The values of the principal angles measured by vom Rath are quoted in the last column of the table of angles.

Cleavage.—There is a good cleavage parallel to  $r'\{\bar{2}01\}$ . The cleaved surfaces gave excellent signal images at exactly 180° from the r' face left on each fragment.

## Volume.

Relative Density.—Five determinations of specific gravity by the immersion method, using methylene iodide and benzene as the immersion liquid, gave the following results:—

I.	Density for	16°·3/4°		2.5578	For	$20^{\circ}/4^{\circ}$			2.5569
II.	,,	17°·1/4°		2.5586	,,	$20^{\circ}/4^{\circ}$			2.5579
III.	,,	17°.6/4°		2.5618	,,	$20^{\circ}/4^{\circ}$			2.5612
IV.	, ,	17°.9/4°	•	2.5619	,,	$20^{\circ}/4^{\circ}$			2.5614
V.	,,	18°·2/4°		2.5591	,,	$20^{\circ}/4^{\circ}$		٠	2.5586
						71.47			215502
						Mean			2.5592

The value accepted for  $20^{\circ}/4^{\circ}$  is therefore 2.559.

Von Groth ('Chemische Krystallographie,' vol. II, p. 545) quotes a value, 2.539, of Topsøe and Christiansen for the specific gravity of this salt; the author is unable to find it in the 1874 memoir of these authors (which deals with the optics), but it is given by Topsøe in his dissertation of 1870.\*

Molecular Volume.— 
$$\frac{M}{d} = \frac{527.52}{2.559} = 206.14$$
.

Molecular Distance Ratios (topic axial ratios).—

$$\chi: \psi: \omega = 6.1677: 8.2598: 4.1786.$$

## Optics.

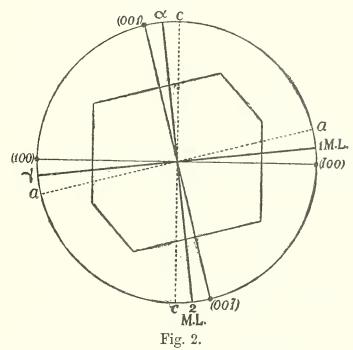
Orientation and Nature of the Optical Ellipsoid.—The plane of the optic axes is the plane of symmetry b {010}. The sign of the double refraction is positive. The first median line, therefore, corresponds to the refractive index  $\gamma$  and the second median line to the index  $\alpha$ .

The orientation of the two median lines in the plane of symmetry was determined with two section-plates ground parallel to that plane with the aid of the cutting and grinding goniometer. The following results were obtained.

Plate 1 . . . . 
$$7^{\circ}$$
 15', Plate 2 . . . .  $7^{\circ}$  40', Mean . . .  $7^{\circ}$  28' with normal to  $c$  {001}.

The position of this extinction direction is behind the normal to c {001}, and it is \* 'Krystallogr.-kem. Unders. over de selensure Salte,' Copenhagen, 1870, p. 10.

the second median line, the first median line being at 90° thereto, as shown in the accompanying fig. 2.



As the normal to  $c\{001\}$  lies 14° 27' in front of the vertical axis c (the morphological axial angle  $\alpha c = 75^{\circ}$  33'), the second median line lies 6° 59' in front of the vertical morphological axis c. The first median line lies to the same extent (6° 59') below the normal to  $\alpha\{100\}$  and 7° 28' above the inclined morphological axis  $\alpha$ .

Very similar positions for the median lines were obtained by Topsøe and Christiansen,\* that for the first median line being given as 6° 57′ above the axis a.

Optic Axial Angle.—Three excellent pairs of section-plates, perpendicular to the first (numbered 1, 2, 3) and second (numbered 1a, 2a, 3a) median lines, were prepared, yielding perfect interference figures in convergent polarised light. They afforded the measurements of 2E (the apparent optic axial angle in air) and of 2H<sub>a</sub> and 2H<sub>o</sub> (the apparent acute and obtuse angles in monobromonaphthalene) recorded in the two following tables; the true optic axial angles calculated from 2H<sub>a</sub> and 2H<sub>o</sub> are given in the penultimate column, and the mean value of the true angle in the last column.

APPARENT Optic Axial Angle in Air, 2E, of KNi Selenate.

Light.	Plate 1.	Plate 2.	Plate 3.	Mean 2E.
Li	129 33	128 40	129 24	129 12
	129 38	128 45	129 29	129 17
	130 16	129 36	130 17	130 3
	131 14	130 26	131 2	130 54
	131 35	130 50	131 34	131 20
	132 6	131 16	131 55	131 46

<sup>\* &#</sup>x27;Ann. Chim. Phys.,' series 5, vol. 1, p. 82 (1874).

DETERMINATION of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2\mathrm{H}_{a}$ .	No. of plate perp. 2 M.L.	Observed $_{2\mathrm{H}_{o}}.$	$rac{ ext{Calculated}}{2 ext{V}_{a}}.$	Mean $2V_a$ .
		o 1.		۰ ,	٠,	0 /
Li	$\frac{1}{2}$	66 7 66 13 66 17	$\begin{array}{c} 1a \\ 2a \\ 3a \end{array}$	95 46 95 37 95 45	$   \begin{array}{c}     72 & 40 \\     72 & 48 \\     72 & 48   \end{array} $	72 45
C	1 2 3	66 5 66 11 66 15	1a 2a 3a	95 42 95 34 95 40	$   \begin{array}{c}     72 & 40 \\     72 & 48 \\     72 & 48   \end{array} $	72 45
Na	1 2 3	65 53 66 2 66 0	1 a 2 a 3 a	95 18 95 9 95 10	$   \begin{array}{c}     72 & 42 \\     72 & 52 \\     72 & 50   \end{array} $	72 48
T1	$\frac{1}{2}$	65 41 65 46 65 48	$egin{array}{c} 1a \ 2a \ 3a \end{array}$	94 54 94 38 94 34	$   \begin{array}{c}     72 & 43 \\     72 & 54 \\     72 & 57   \end{array} $	72 51
Cd	1 2 3	65 31 65 38 65 39	$egin{array}{c} 1a \\ 2a \\ 3a \end{array}$	94 35 94 20 94 14	$   \begin{array}{c}     72 & 44 \\     72 & 56 \\     73 & 0   \end{array} $	72 53
F {	$\frac{1}{2}$	$\begin{array}{ccc} 65 & 20 \\ 65 & 31 \\ 65 & 29 \end{array}$	$egin{array}{c} 1a \ 2a \ 3a \end{array}$	94 15 93 56 93 51	$   \begin{array}{ccc}     72 & 45 \\     73 & 1 \\     73 & 2   \end{array} $	72 56

The values obtained by Topsøe and Christiansen\* were, for 2E 129° 56′ and for  $2V_a$  72° 56′.

Dispersion of the Median Lines.—This is exceedingly small, namely, about 7' only. The direction is such that the first median line is nearer to the axis a by 7' for red C hydrogen light than for greenish blue F hydrogen light. It was determined by observations with the section-plates 2 and 3 immersed in monochlorbenzene, the refractive index of which, 1.5248 for D-light, is nearly identical with the mean index of the crystals.

Effect of Temperature on Optic Axial Angle.—The apparent optic axial angle in air 2E increases with rise of temperature. The amount of the increase was determined with section 3, and proved to be 3° 16′ for a rise of 50° (from 18° to 68°) of temperature.

Refractive Indices.—Six 60° prisms were prepared with the aid of the cutting and grinding goniometer, each to yield two of the three indices directly, the bisecting plane and refractive edge being parallel respectively to a principal plane and principal axis of the optical ellipsoid. Four different values for each index were thus obtained. The mean results are given in the accompanying table.

<sup>\* &#</sup>x27;Ann. Chim. Phys.,' series 5, vol. 1, p. 83 (1874).

Light.	α.	β.	γ.
Li	$1 \cdot 5142$ $1 \cdot 5147$ $1 \cdot 5181$ $1 \cdot 5212$ $1 \cdot 5232$ $1 \cdot 5251$ $1 \cdot 5314$	$1 \cdot 5232$ $1 \cdot 5237$ $1 \cdot 5272$ $1 \cdot 5305$ $1 \cdot 5325$ $1 \cdot 5344$ $1 \cdot 5407$	1.5387 $1.5392$ $1.5427$ $1.5464$ $1.5486$ $1.5507$ $1.5571$

Mean of  $\alpha$ ,  $\beta$ , and  $\gamma$  for Na light = 1.5293.

 $\alpha$  = Vibration direction parallel to second median line, 6° 59' in front of axis c.

 $\beta =$  ,, ,, ,, symmetry axis b.

 $\gamma = 0.5$ , , , , first median line, 7° 28' above axis a.

Double refraction,  $Na_{\gamma-\alpha} = 0.0246$ .

General formula for  $\beta$ , corrected to a vacuum:—

$$\beta = 1.5043 + \frac{1.034.256}{\lambda^2} - \frac{7.821.960.000.000}{\lambda^4} + \dots$$

The  $\alpha$  indices are equally well reproduced by the formula if the constant 1.5043 is diminished by 0.0092, and the  $\gamma$  indices if it is increased by 0.0156.

Observations at 70° indicated that the refractive indices of potassium nickel selenate diminish by about 0.0018 for a rise of 55° of temperature.

The values of Topsoe and Christiansen\* for the refractive indices were: for  $\beta$ , line C 1.5207, line D 1.5248, line F 1.5315; the  $\alpha$  and  $\gamma$  values were only obtained indirectly, and for line D only; they are given as 1.5199 and 1.5339.

Axial Ratios of the Optical Ellipsoid.—These values work out as under:—

Indicatrix . . . .  $\alpha:\beta:\gamma=0.9940:1:1.0101$ . Velocity ellipsoid . . a:b:c=1.0060:1:0.9900.

Molecular Optical Constants.—The values of these constants, calculated by both the formulæ of Lorenz and of Gladstone and Dale, are given in the next table.

	Axis of optical indicatrix	α.	β.	γ.
LORENZ . '' .,' .,' .,' GLADSTONE	Specific refraction, $\frac{n^2-1}{(n^2+2)d}=n$ $\begin{cases} C\\G \end{cases}$ Molecular refraction, $\frac{n^2-1}{n^2+2}\cdot\frac{M}{d}=m$ . $\begin{cases} C\\G \end{cases}$ Specific dispersion, $\mathfrak{n}_G-\mathfrak{n}_C$ Molecular dispersion, $\mathfrak{m}_G-\mathfrak{m}_C$	$0.0032 \\ 1.68$	0.1195 $0.1227$ $63.04$ $64.75$ $0.0032$ $1.71$ $107.96$	$0.1225 \\ 0.1258 \\ 64.60 \\ 66.37 \\ 0.0033 \\ 1.77 \\ 111.10$

Mean molecular refraction (GLADSTONE),  $\frac{1}{3}(\alpha + \beta + \gamma) = 108 \cdot 39$ .

<sup>\* &#</sup>x27;Ann. Chim. Phys.,' series 5, vol. 1, p. 82 (1874).

# Rubidium Nickel Selenate, $Rb_2Ni(SeO_4)_2 . 6H_2O$ .

# Morphology.

The crystals of this salt do not appear to have been hitherto investigated. They are bright green in colour, resembling the potassium salt, but are somewhat richer in faces. About 20 crops were successively obtained, three of which were of special excellence for goniometrical purposes.

Ten small crystals were measured, selected from the three crops above mentioned, the crystals of which were most free from striation. The individuals measured were especially perfect, as will be obvious from the close agreement between the observed and calculated values in the accompanying table of angles representing the results of the measurements.

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

Ratios of Axes.—

a:b:c=0.7395:1:0.5031.

 $Axial\ Angle.$ — $\beta = 105^{\circ}\ 20'.$ 

Forms Observed.—b {010}, c {001}, p {110}, q {011}, r'{ $\bar{2}$ 01}, and o'{ $\bar{1}$ 11}.

Habit.—More or less tabular parallel to c {001}, the commonest type being represented in fig. 3; occasionally the tables become so thick as to affect a short prismatic habit parallel to p {110}.

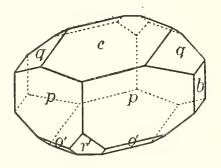


Fig. 3.

The  $q\{011\}$  faces were relatively more prominent on the crystals of this salt, and the  $c\{001\}$  faces correspondingly less so, than in the case of the crystals of the potassium salt. The c faces were generally, however, still to some extent the larger. The faces of the primary prism  $p\{110\}$  were invariably predominant. Several of the crops consisted of crystals showing good little faces of the clinopinakoid  $b\{010\}$ , and very narrow faces of  $o'\{\overline{1}11\}$  on each side of the small faces of  $v'\{\overline{2}01\}$ , which latter were shown by most of the crystals of all the crops prepared.

Cleavage.—There is a good cleavage parallel to  $r'\{\bar{2}01\}$ . No trace of any other cleavage was observed.

Interfacial Angles of Rubidium Nickel Selenate.

$ \begin{cases} cs' &= (001): (\bar{1}01) \\ s'r' &= (\bar{1}01): (\bar{2}01) \\ r'a &= (\bar{2}01): (\bar{1}00) \\ r'c &= (\bar{2}01): (00\bar{1}) \end{cases} $	Limits.	Mean observed.	Calculated.	Diff.
qp = (011) : (110) 18	Limits.  Limits.  Limits.  3 50- 64 7  — 61 10  — 65 49-116 10  — 68 51-109 9  65 46- 25 58  64 2- 64 14  88 9-128 21  — 7  — 7  — 7  — 7  — 7  — 7  — 7  —		74 40 45 36 29 4 63 58 38 38·5 25 19·5 41 22 116 2 35 30·5 19 28 35 1·5 29 27 25 2·5 71 1 108 59 25 53 128 14 48 49 27 25 76 14 34 50 68 56 34 40 42 54 * 57 34 44 52 102 26 54 18 15 56 70 14 19 46 65 12 24 48 49 36 38 9 86 34 55 17 93 26 45 21 26 42 36 44 63 26	Diff.
$ \begin{cases} ps' &= (110) : (10\overline{1}) \\ pq &= (110) : (0\overline{1}\overline{1}) \end{cases} $ $ \begin{cases} r'o' &= (\overline{2}01) : (\overline{1}11) \\ o'p &= (\overline{1}11) : (110) \\ pr' &= (110) : (20\overline{1}) \end{cases} $ 1 $ \begin{cases} 1 &= 6 \\ 6 &= 6 \end{cases} $	6 27-116 43 34 40- 34 56 92 45- 92 56 52 11- 52 28 27 27-127 50	116 35 34 47 92 51 52 20:5 127 38	71 13 116 34 34 52 92 47·5 52 20·5 127 39·5	1 5 3·5 0 1·5

#### Volume.

Relative Density.—Four determinations by the immersion method yielded the following values:—

I.	Density for	16°.9/4°	•		2.8579	$\operatorname{For}$	$20^{\circ}/4^{\circ}$	•		2.8570
II.	,,	17°.3/4°	•		2.8577	,,	$20^{\circ}/4^{\circ}$		٠	2.8569
III.	,,	17°·3/4°			2.8551	,,	$20^{\circ}/4^{\circ}$			2.8543
IV.	,,	18°.9/4°			2.8556	,,	$20^{\circ}/4^{\circ}$			2.8553
										<del></del>
							Mean			2.8559

Accepted value for 20°/4°, 2.856. This appears to be the first determination of the specific gravity of rubidium nickel selenate.

$$\label{eq:Molecular_volume} \textit{Molecular Volume.} - \frac{M}{d} = \frac{619 \cdot 62}{2 \cdot 856} = 216 \cdot 96.$$

Molecular Distance Ratios (topic axial ratios).—

$$\chi: \psi: \omega = 6.2533:8.4561:4.2542.$$

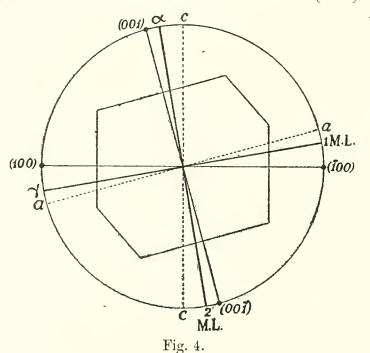
# Optics.

Orientation and Nature of Optical Ellipsoid.—The plane of the optic axes is the symmetry plane b {010}. The double refraction is of positive sign, the first median line corresponding to the refractive index  $\lambda$  and the second median line to  $\alpha$ .

Extinction determinations with two section-plates parallel to the symmetry plane afforded the following indications of the direction of one of the two principal axes of the optical ellipsoid (the median lines) lying in that plane.

Extinction Direction in the Symmetry Plane.

Plate 1 . . . . 
$$5^{\circ}$$
 34', Plate 2 . . . .  $5^{\circ}$  8', Mean . . .  $5^{\circ}$  21' with normal to  $c$  {001}.



This direction is behind the normal to the basal plane  $c_i\{001\}$ , towards the vertical morphological axis  $c_i$ , and it is the second median line. Fig. 4 will make the position clear. As the morphological axial angle  $ac_i$  is  $74^\circ$  40', and the angle between the normal to  $c_i\{001\}$  and the vertical axis  $c_i$  is consequently 15° 20', the second median line lies 9° 59' in front of the vertical axis  $c_i$ , in the obtuse angle of the morphological axes  $a_i$  and  $a_i$ . The first median line lies 5° 21' above the inclined morphological axis  $a_i$ , also in the obtuse angle  $ac_i$ , and 9° 59' below the normal to  $a_i$  {100}.

Optic Axial Angle.—Three excellent pairs of section-plates were ground perpendicular to the first (1, 2, 3) and second (1a, 2a, 3a), median lines, and they afforded good interference figures in monobromonaphthalene, from which the measurements of the acute and obtuse angles  $2H_a$  and  $2H_o$  and the calculated results for the true angle  $2V_a$  recorded in the accompanying table were derived. The apparent optic axial angle in air 2E is so large that it is not possible to measure it, the interference brushes and innermost rings disappearing before the brushes can be brought quite to the cross-wires of the polarising goniometer.

Rubidium Nickel Selenate.

Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$ .	No. of plate perp. 2 M.L.	Observed $2\mathrm{H}_{o}$ .	Calculated $2V_a$ .	$_{2\mathrm{V}_{a}.}^{\mathrm{Mean}}$
		0 /		0 /	٥ /	۰ ,
Li	$\frac{1}{2}$	74  36 $74  38 $ $74  53$	$egin{array}{c} 1a \ 2a \ 3a \end{array}$	87 37 87 52 87 53	$   \begin{array}{c}     82 & 24 \\     82 & 18 \\     82 & 27   \end{array} $	82 23
C	1 2 3	74 33 74 36 74 50	1a $2a$ $3a$	87 36 87 50 87 51	$   \begin{array}{c}     82 & 22 \\     82 & 17 \\     82 & 26   \end{array} $	82 22
Na	$\begin{array}{c} 1 \\ 2 \\ 3 \end{array}$	74 14 74 19 74 14	$egin{array}{c} 1a \ 2a \ 3a \end{array}$	87 29 87 30 87 38	$   \begin{array}{c}     82 & 14 \\     82 & 16 \\     82 & 9   \end{array} $	82 13
Tl	1 2 3	73 52 73 58 73 47	1 <i>a</i> 2 <i>a</i> 3 <i>a</i>	87 21 87 9 87 14	$   \begin{array}{ccc}     82 & 4 \\     82 & 13 \\     82 & 4   \end{array} $	8:2 7
Cd	$\frac{1}{2}$	73 36 73 36 73 33	1a $2a$ $3a$	87 12 86 55 87 0	$ \begin{array}{ccc} 81 & 58 \\ 82 & 7 \\ 82 & 2 \end{array} $	82 3
F	$\frac{1}{2}$	73 23 73 22 73 18	1a 2a 3a	87 5 86 39 86 46	$ \begin{array}{c} 81 & 52 \\ 82 & 5 \\ 81 & 59 \end{array} $	81 58

Dispersion of the Median Lines.—The median lines show practically no dispersion. Section 1 showed 3' in one direction and section 3 showed 2' in the other direction,

while section 2 exhibited no measurable amount of dispersion. The section-plates were immersed during these observations in methyl salicylate, the refractive index of which liquid (1.5363) is not far from the mean index of the crystals.

Refractive Indices.—Six 60°-prisms were employed, ground so that each afforded directly two indices,  $\alpha$  and  $\beta$ , or  $\beta$  and  $\gamma$ , or  $\alpha$  and  $\gamma$ , the refracting edge not only being parallel to a principal axis of the optical ellipsoid, but the bisecting plane being also parallel to a principal plane of the ellipsoid. The mean results for the four independent values of each index thus obtained are given in the accompanying table.

REFRACTIVE	Indices	of	Rubidium	Nickel	Selenate.

Light.	α.	β.	γ.
Li	1.5161 $1.5166$ $1.5198$ $1.5231$ $1.5248$ $1.5268$ $1.5335$	$egin{array}{c} 1 \cdot 5253 \\ 1 \cdot 5258 \\ 1 \cdot 5291 \\ 1 \cdot 5325 \\ 1 \cdot 5342 \\ 1 \cdot 5362 \\ 1 \cdot 5429 \\ \hline \end{array}$	$1 \cdot 5351$ $1 \cdot 5356$ $1 \cdot 5390$ $1 \cdot 5424$ $1 \cdot 5443$ $1 \cdot 5466$ $1 \cdot 5534$

Mean of  $\alpha$ ,  $\beta$ , and  $\gamma$  for Na light = 1.5293.

 $\alpha$  = Vibration direction parallel to second median line, 9° 59′ in front of axis c.

 $\beta =$ ,, ,, ,, symmetry axis b.

 $\gamma =$  ,, ,, first median line, 5° 21' above axis a.

Double refraction,  $Na_{\gamma-\alpha} = 0.0192$ .

General formula for  $\beta$ , corrected to a vacuum:—

$$\beta = 1.5103 + \frac{760688}{\lambda^2} - \frac{3270.190000000}{\lambda^4} + \dots$$

The  $\alpha$  indices are also reproduced by the formula if the constant 1.5103 is diminished by 0.0093, and the  $\gamma$  indices if it is increased by 0.0099.

Observations at 70° indicated that the refractive indices diminished with rise of temperature, to the extent of 0.0017 for 55° rise of temperature.

Axial Ratios of the Optical Ellipsoid.—The values for the optical indicatrix and optical velocity ellipsoid are respectively as follows:—

 $\alpha:\beta:\gamma=0.9939:1:1.0065.$ 

a : b : c = 1.0061 : 1 : 0.9936.

Molecular Optical Constants.—The values of the Lorenz and the Gladstone and Dale constants are given in the accompanying table.

	Axis of optical indicatrix .	• •	α.	β.	γ.
LORENZ	Specific refraction, $\frac{n^2-1}{(n^2+2) d} = \mathfrak{n}$	$\left\{ \begin{smallmatrix} \mathrm{C} \\ \mathrm{G} \end{smallmatrix} \right.$	0·1059 0·1088	$0.1074 \\ 0.1104$	0·1091 0·1121
,,	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{\mathrm{M}}{d} = \mathrm{m}$ .	$\left\{ egin{array}{l} \mathrm{C} \\ \mathrm{G} \end{array}  ight.$	$65 \cdot 59 \\ 67 \cdot 39$	66 · 57 68 · 38	67 · 61 69 · 47
21 22	Specific dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$ Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$		0.0029 $1.80$	0.0030 1.81	0.0030 1.86
GLADSTONE	Molecular refraction, $\frac{n-1}{d}$ M	. С	112.08	114.07	116:20

Mean molecular refraction (GLADSTONE),  $\frac{1}{3}(\alpha + \beta + \gamma) = 114 \cdot 12$ .

Casium Nickel Sclenate, Cs<sub>2</sub>Ni (SeO<sub>4</sub>)<sub>2</sub>. 6H<sub>2</sub>O.

# Morphology.

No previous measurements or description of this salt appear to have been made. It forms bright emerald green crystals of perfect transparency, possessing faces of high reflecting power. About thirty crops were prepared, derived from two distinct preparations.

Twelve small crystals, in several cases no larger than a pin's head, were measured, selected from four different crops.

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

Ratios of Axes.—a:b:c = 0.7288:1:0.4993.

Axial Angle.— $\beta = 106^{\circ} 11'$ .

Forms Observed.—a {100}, b {010}, c {001}, p {110}, q {011}, r' { $\overline{2}$ 01}, and o'{ $\overline{1}$ 11}.

Habit.—Very characteristic. Prismatic parallel to the inclined axis a, the prism being formed by the broad and elongated faces of q {011} and the narrower elongated faces of the basal plane c {001}, as shown in fig. 5.

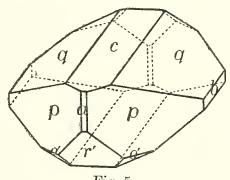


Fig. 5.

The facial development and planeness, in the cases of the measured crystals, were exceptionally perfect, the signal reflections being so sharp and true that in the cases

# Interfacial Angles of Cæsium Nickel Selenate.

$\begin{cases} ac &= (100) : (001) \\ as &= (100) : (101) \\ sc &= (101) : (001) \\ cr' &= (001) : (\overline{2}01) \\ cs' &= (\overline{1}01) : (\overline{2}01) \\ s'r' &= (\overline{1}01) : (\overline{2}01) \\ r'a &= (\overline{2}01) : (\overline{1}00) \\ r'c &= (\overline{2}01) : (00\overline{1}) \end{cases}$ $\begin{cases} ap &= (100) : (110) \\ pp' &= (110) : (120) \\ p'b &= (120) : (010) \\ pp''''b &= (130) : (010) \\ pp''''b &= (110) : (1\overline{1}0) \end{cases}$ $\begin{cases} cq &= (001) : (\overline{1}10) \\ q\bar{b} &= (011) : (010) \\ q\bar{b} &= (011) : (010) \end{cases}$	14 ————————————————————————————————————	64 42- 65 4   64 42- 65 4   114 55-115 19   54 58- 55 6 69 50- 70 0  25 33- 25 44 64 17- 64 29	115 5	73 49 44 51 28 58 64 54 39 11 25 43 41 17 115 6 34 58 19 28 35 34 29 33 25 29 * 69 56	
$\begin{cases} oq &= (111):(011) \\ aq &= (100):(011) \\ qo' &= (011):(\bar{1}11) \\ o'a &= (\bar{1}11):(\bar{1}00) \end{cases}$ $\begin{cases} co &= (001):(111) \\ op &= (111):(110) \\ cp &= (001):(11\bar{1}0) \\ po' &= (110):(11\bar{1}) \\ o'c &= (11\bar{1}):(00\bar{1}) \end{cases}$ $\begin{cases} bn &= (010):(121) \\ no &= (121):(111) \\ bo &= (010):(\bar{1}11) \\ os &= (111):(\bar{1}01) \end{cases}$ $\begin{cases} bo' &= (010):(\bar{1}11) \\ o's' &= (\bar{1}11):(\bar{1}01) \\ o'o' &= (\bar{1}11):(\bar{1}\bar{1}1) \end{cases}$ $\begin{cases} sq &= (101):(011) \\ qp &= (011):(\bar{1}0\bar{1}) \\ pq &= (\bar{1}10):(0\bar{1}1) \end{cases}$ $\begin{cases} s'q &= (\bar{1}01):(011) \\ qn &= (011):(110) \\ qp &= (011):(110) \end{cases}$	1 		64 23	25 37  48 2 27 25 75 27 35 19 69 14  34 23 42 25  *  58 0 45 12  54 51 15 45 70 36 19 24 41 49 22 37 55 87 36 54 29 92 24 45 39 92 24 45 39 26 37 36 24 63 1 71 20	
$\begin{cases} ps' &= (110) : (10\bar{1}) \\ pq &= (110) : (0\bar{1}\bar{1}) \\ r'o' &= (\bar{2}01) : (\bar{1}11) \\ o'p &= (\bar{1}11) : (110) \\ pr' &= (110) : (20\bar{1}) \end{cases}$ $Total number of measurements$	10 12 23 472	116 56-117 6 34 51- 35 14 92 48- 93 6 51 50- 52 10	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	116 59 35 4 92 57 51 59	1 1 3 2

of practically all the measured angles the agreement between the observed and calculated values lies within two minutes, as will be seen from the table. The habit defined above is essentially characteristic of the salt, the vast majority of the crystals in all the 30 crops grown consisting of crystals of this type. Usually also only the forms q {011} and c {001}, forming the prism, and smaller faces of p {110}, forming the ends, are visible. Closer inspection, however, reveals small faces of r' { $\bar{2}01$ }, still more minute ones of o' { $\bar{1}11$ }, and occasionally traces of the primary orthopinakoid a {100}, at the ends; while the sharper long edges of the prism q {011} are blunted by long but very narrow faces, often mere lines, of the clinopinakoid b {010}. The signal images from the q and p faces were wonderfully sharply defined and perfect on all the crystals measured, and on most of these crystals, selected for their perfection, the other faces just referred to were somewhat more prominently developed than usual, and gave excellent reflections.

Some larger crystals were obtained in several of the crops which were somewhat tabular parallel to  $c\{001\}$ , owing to the faces of the basal plane being more extensively developed; the faces of  $r'\{\bar{2}01\}$  were also frequently relatively larger on these crystals.

Cleavage.—A good cleavage is developed parallel to  $r'\{\bar{2}01\}$ . There is no facility for cleavage parallel to any other direction.

#### Volume.

Relative Density.—Five determinations by the immersion method gave the following results:—

I.	Density for	16°·2/4°		3.1137	For	$20^{\circ}/4^{\circ}$				3.1125
II.	>>	16°·3/4°		3.1130	,,	$20^{\circ}/4^{\circ}$	•			3.1118
III.	2.2	16°.6/4°		3.1186	,,	$20^{\circ}/4^{\circ}$				3.1175
IV.	,,	17°.0/4°		3.1149	, ,	$20^{\circ}/4^{\circ}$		•	٠	3.1140
V.	,,	17°·1/4°		3.1134	"	$20^{\circ}/4^{\circ}$		•		3.1125
						Mean				3.1137

The value accepted for  $20^{\circ}/4^{\circ}$  is 3.114.

The specific gravity of cæsium nickel selenate does not appear to have been previously determined.

Molecular Volume.—
$$\frac{M}{d} = \frac{713.62}{3.114} = 229.17$$
.

Molecular Distance Ratios (topic axial ratios).—

 $\chi: \psi: \omega = 6.3317: 8.6878: 4.3378.$ 

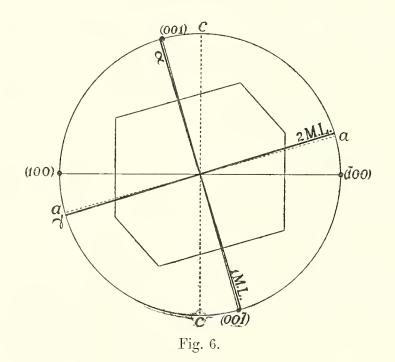
#### Optics.

Nature and Orientation of the Optical Ellipsoid.—The plane of the optic axes is the symmetry plane b {010}, as usual for this series of double salts. But the sign of the double refraction is by exception negative, as was also found to be the case with cæsium nickel sulphate. Extinction determinations made with two section-plates ground parallel to the symmetry plane afforded the following values:—

Extinction Direction in the Symmetry Plane.

Plate 1 . . . . 
$$0^{\circ}$$
 55', Plate 2 . . .  $0^{\circ}$  24', Mean . .  $0^{\circ}$  40' in front of normal to  $c$  {001}. .

This direction, nearly normal to the basal plane, is in this salt by exception the first median line, instead of the second median line as is usual in the series; it corresponds, however, as usual, to the refractive index  $\alpha$ , while the other extinction at right angles to it in the symmetry plane corresponds to  $\gamma$  and is the second median line. This will be clear from fig. 6.



As the morphological axial angle ac is 73° 49′, and the angle between the normal to c {001} and the vertical axis c is consequently 16° 11′, the first median line lies 16° 51′ in front of the vertical axis c in the obtuse axial angle ac. The second median line lies 0° 40′ below the inclined axis a in the acute morphological axial angle ac.

Optic Axial Angle.—Three section-plates, 1, 2, and 3, were ground perpendicular to the first median line, and three others, 1a, 2a, and 3a, perpendicular to the second median line. The optic axial angle is so large that 2E, the apparent angle in air, is

not measurable. The apparent acute and obtuse angles,  $2H_a$  and  $2H_o$ , are readily measurable in bromonaphthalene, and the results of the measurements, together with the calculated values of the true optic axial angle  $2V_a$  derived therefrom, are given in the accompanying table.

Casium Nickel Selenate.

Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$ .	No. of plate perp. 2 M.L.	Observed $2\mathrm{H}_{o}$ .	Calculated $2V_a$ .	$\begin{array}{c} \mathrm{Mean} \\ 2\mathrm{V}_{\alpha}. \end{array}$
Li	1 2 3	76 15 75 50 76 15	1a $2a$ $3a$	89 14 89 2 88 35	82 38 82 28 82 58	82 41
C	$\frac{1}{2}$	76 13 75 49 76 14	$\begin{array}{c} 1a \\ 2a \\ 3a \end{array}$	89 8 88 57 88 30	$   \begin{array}{c}     82 & 40 \\     82 & 30 \\     83 & 0   \end{array} $	82 43
Na	$\frac{1}{2}$	$76   7 \ 75   45 \ 76   9$	1a $2a$ $3a$	88 4 88 1 87 45	$   \begin{array}{c}     83 & 8 \\     82 & 56 \\     83 & 20   \end{array} $	83 8
T1	$\begin{array}{c}1\\2\\3\end{array}$	$ \begin{array}{ccc} 76 & 1 \\ 75 & 40 \\ 76 & 3 \end{array} $	1a 2a 3a	87 12 87 4 87 17	$   \begin{array}{c}     83 & 32 \\     83 & 22 \\     83 & 30   \end{array} $	83 28
Cd {	1 2 3	75 57 75 35 75 59	1a $2a$ $3a$	86 55 86 49 86 42	$   \begin{array}{c}     83 & 38 \\     83 & 27 \\     83 & 46   \end{array} $	83 37
F	1 2 3	75 53 75 29 75 49	$egin{array}{c} 1a \\ 2a \\ 3a \end{array}$	86 42 86 28 86 20	$   \begin{array}{c}     83 & 42 \\     83 & 34 \\     83 & 52   \end{array} $	83 43

Dispersion of the Median Lines.—The dispersion of the two median lines in the symmetry plane is such that the first median line lies about 10' nearer to the vertical axis c for greenish blue F light than for red C light. The determinations were made with sections 1 and 3 immersed in oil of anis, the refractive index of which liquid (1.5540) is not far removed from that of the crystal; the actual amounts observed with the two sections were respectively 12' and 8'.

Refractive Indices.—Six 60°-prisms were ground, each with its bisecting plane parallel to a principal plane of the optical ellipsoid and its refracting edge parallel to one of the principal axes of the ellipsoid, so as to yield two refractive indices directly; the directions were so chosen that each of the three indices  $\alpha$ ,  $\beta$  and  $\gamma$ , was afforded by four different prisms. The results were very concordant, and the final mean values are recorded in the next table.

Light.	a.	β.	γ.
Li	1.5358 $1.5363$ $1.5395$ $1.5428$ $1.5447$ $1.5467$ $1.5533$	1.5412 $1.5417$ $1.5450$ $1.5483$ $1.5504$ $1.5525$ $1.5589$	1.5451 $1.5456$ $1.5489$ $1.5526$ $1.5547$ $1.5568$ $1.5631$

#### REFRACTIVE Indices of Cæsium Nickel Selenate.

Mean of  $\alpha$ ,  $\beta$ , and  $\gamma$  for Na light = 1.5445.

 $\alpha$  = Vibration direction parallel to first median line, 16° 51′ in front of axis c.

eta = ,, , , , symmetry axis b.

 $\gamma =$  ,, ,, second median line, 0° 40′ below axis a. Double refraction,  $Na_{\gamma-\alpha} = 0.0094$ .

General formula for the intermediate refractive index  $\beta$ , corrected to a vacuum (correction + 0.0004):—

$$\beta = 1.5252 + \frac{837\ 474}{\lambda^2} - \frac{4\ 729.540\ 000\ 000}{\lambda^4} + \dots$$

The  $\alpha$  indices are also reproduced very closely by the formula if the constant 1.5252 is diminished by 0.0055, and the  $\gamma$  indices if the constant is increased by 0.0040.

Observations at 70° showed that the refractive indices of cæsium nickel selenate are diminished by 0.0013 for  $\alpha$ , 0.0016 for  $\beta$ , and 0.0018 for  $\gamma$  for 55° rise of temperature.

Axial Ratios of the Optical Ellipsoid.—The calculated values for both the optical indicatrix and the optical velocity ellipsoid are given below:—

 $\alpha:\beta:\gamma = 0.9964:1:1.0025.$  $\alpha:\mathfrak{h}:\mathfrak{r} = 1.0036:1:0.9975.$ 

Molecular Optical Constants.—These work out as under:—

	Axis of optical indicatrix	α.	β.	γ.
Lorenz	Specific refraction, $\frac{n^2-1}{(n^2+2) d} = \mathfrak{n}$ . $\begin{cases} \mathbb{C} \\ \mathbb{G} \end{cases}$ Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{\mathbb{M}}{d} = \mathfrak{m}$ . $\begin{cases} \mathbb{C} \\ \mathbb{G} \end{cases}$	0·1002 0·1028	0·1010 0·1037	0·1016 0·1043
,,	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m$ . $\begin{cases} C \\ G \end{cases}$	71·49 73·37	$\begin{array}{c} 72 \cdot 09 \\ 73 \cdot 98 \end{array}$	$72 \cdot 52 \\ 74 \cdot 44$
"	Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$ Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$	$0.0026 \\ 1.88$	0·0027 1·89	$0.0027 \\ 1.92$
GLADSTONE	Molecular refraction, $\frac{n-1}{d}$ M C	122.90	124.14	125.03

Mean molecular refraction (GLADSTONE),  $\frac{1}{3}(\alpha + \beta + \gamma) = 124.02$ .

#### Ammonium Nickel Sclenate (NH<sub>4</sub>)<sub>2</sub> Ni (SeO<sub>4</sub>)<sub>2</sub>. 6H<sub>2</sub>O.

#### Morphology.

The crystals of ammonium nickel selenate were goniometrically investigated by Topsøe\* in the year 1870, and as regards their optics were included, like the potassium salt, by Topsøe and Christiansen† in their well-known research of 1874.

The crystals are bright green in colour, very like the potassium salt, but more generally perfectly transparent.

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

Ratios of Axes.—a:b:c=0.7395:1:0.5048. Values of Topsøe, 0.7378:1:0.5042.

Axial Angle.— $\beta = 106^{\circ} 17'$ . Value of Topsøe,  $106^{\circ} 19'$ .

Forms Observed.—b {010}, c {001}, p {110}, p'{120}, q {011}, r'{ $\overline{2}$ 01}, and o'{ $\overline{1}$ 11}. The same forms, and no others, were observed by Topsøe.

*Habit.*—More or less tabular parallel to  $c\{001\}$ , as shown in fig. 7.

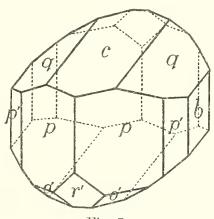


Fig. 7.

Eleven small crystals belonging to five different crops were measured, the crops being selected from the thirty or more prepared for their greater freedom from striation. The results are given in the accompanying table of angles.

A large proportion of the crystals showed no other forms than  $c \{001\}$ ,  $q \{011\}$ ,  $p \{110\}$ , and  $r'\{\bar{2}01\}$ . Certain crops, however, exhibited characteristically in addition excellent little faces of the clinopinakoid  $b \{010\}$ , with occasional development of the prism  $p'\{120\}$  as a fairly broad face, and of the hemipyramid  $o'\{\bar{1}11\}$  as narrow faces blunting the pc edges. The faces of  $q \{011\}$  were particularly well formed, usually affording single sharp images of the signal. The b faces and r' faces were also similarly excellent when present. The faces of  $c \{001\}$  and  $p \{110\}$ , however, were generally much striated. The measured crystals were selected on account of their exceptional freedom from this defect.

<sup>\* &#</sup>x27;Kryst-kem. Unders. o. d. selens. Salte, Dissertation,' Copenhagen, 1870, p. 39.

<sup>† &#</sup>x27;Ann. Chim. Phys.' (1874), series 5, vol. 1, p. 81.

# Interfacial Angles of Ammonium Nickel Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of Topsøe.
$\begin{cases} ac = (100) : (001) \\ as = (100) : (101) \\ sc = (101) : (001) \end{cases}$		· / • /	· /	$     \begin{array}{ccccccccccccccccccccccccccccccccc$	<u>'</u>	73 41
$\begin{cases} cr' = (001) : (\bar{2}01) \\ cs' = (001) : (\bar{1}01) \end{cases}$	17 —	64 42- 64 52	64 46	$\begin{array}{ccc} 64 & 46 \\ 39 & 0 \end{array}$	0	64 50
$ \begin{vmatrix} s'r' &= (\bar{1}01) : (\bar{2}01) \\ r'a &= (\bar{2}01) : (\bar{1}00) \\ r'c &= (\bar{2}01) : (00\bar{1}) \end{vmatrix} $	$\frac{-}{17}$	115 8-115 18	115 13	$\begin{array}{ccc} 25 & 46 \\ 41 & 31 \\ 115 & 14 \end{array}$	<u></u>	<u> </u>
$\begin{cases} ap = (100) : (110) \\ pp' = (110) : (120) \\ p'b = (120) : (010) \end{cases}$	$\frac{}{2}$	19 20- 19 34 35 7- 35 11	19 27 35 9	$   \begin{array}{rrr}     35 & 22 \\     19 & 28 \\     35 & 10   \end{array} $		19 25 —
$\begin{cases} pp''' = (110) : (130) \\ p'''b = (130) : (010) \\ pb = (110) : (010) \end{cases}$	$\frac{-}{40}$	54 25- 54 48	54 38	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	  	
$\begin{cases} pp &= (110) : (1\bar{1}0) \\ cq &= (001) : (011) \\ q\bar{b} &= (011) : (010) \end{cases}$	15 42 44	70 36 - 70 58 $25 44 - 25 57$ $64 4 - 64 16$	$ \begin{array}{cccc} 70 & 45 \\ 25 & 51 \\ 64 & 9 \end{array} $	$\begin{array}{c c} 70 & 44 \\ 25 & 51 \\ * \end{array}$	1 0	70 36 25 49
$ \begin{cases}     ao = (100):(111) \\     oq = (111):(011) \end{cases} $	_	— — —-	— —	48 10 27 13	_	
$\begin{cases} aq = (100) : (011) \\ qo' = (011) : (\bar{1}11) \\ o'a = (\bar{1}11) : (\bar{1}00) \end{cases}$				75 23 35 7 69 30		_ 
$\begin{cases} co = (001): (111) \\ op = (111): (110) \\ cp = (001): (110) \end{cases}$	$\frac{-}{42}$		76 47	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	_	- 76 51
$\begin{cases} cp &= (001): (110) \\ po' &= (110): (11\overline{1}) \\ o'c &= (11\overline{1}): (00\overline{1}) \\ pc &= (110): (00\overline{1}) \end{cases}$	11 11 32	57 52- 58 5 45 8- 45 21 103 7-103 24	57 57 45 15 103 13	58 0 45 13 103 13	3 2 0	58 5 45 4
$\begin{cases} bn &= (010): (121) \\ no &= (121): (111) \\ bo &= (010): (111) \end{cases}$	_ 		=	54 31 15 52 70 23		
$\begin{cases} os &= (111) : (101) \\ bo' &= (010) : (\bar{1}11) \\ \bar{1}11 & \bar{1}11 \end{cases}$	12	65 0- 65 10	65 5	19 37 65 2	3	
$\begin{cases} o's' = (\bar{1}11) : (\bar{1}01) \\ o'o' = (\bar{1}11) : (\bar{1}\bar{1}1) \end{cases}$	6	49 46- 49 56	49 51	24 58 49 56	5	
$\begin{cases} sq &= (101): (011) \\ qp &= (011): (\bar{1}10) \\ ps &= (\bar{1}10): (\bar{1}0\bar{1}) \\ pq &= (\bar{1}10): (0\bar{1}\bar{1}) \end{cases}$	33  38	87 10- 87 29 	87 17	37 56 87 20 54 44 92 40	3 — 3	87 23 —
$\begin{cases} pq &= (110) : (011) \\ s'q &= (\bar{1}01) : (011) \\ qn &= (011) : (121) \end{cases}$		——————————————————————————————————————	92 43	$\begin{array}{c} 92 & 40 \\ 45 & 37 \\ 26 & 28 \end{array}$	- -	
$\begin{cases} p = (011) \cdot (121) \\ pp = (121) \cdot (110) \\ pp = (011) \cdot (110) \\ ps' = (110) \cdot (10\overline{1}) \end{cases}$	41	62 32- 62 49	62 41	36 16 62 44	<del>-</del> 3	62 44
$pq = (110) : (0\bar{1}\bar{1})$	41	117 11–117 29	117 19	71 39 117 16	3	_
$\begin{cases} r'o' = (\bar{2}01) : (\bar{1}11) \\ o'p = (\bar{1}11) : (110) \\ pr' = (110) : (20\bar{1}) \end{cases}$	10	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$egin{array}{cccc} 35 & 15 \ 92 & 17 \ 52 & 25 \ \end{array}$	$\begin{array}{cccc} 35 & 16 \\ 92 & 22 \\ 52 & 22 \end{array}$	1 5 3	<u> </u>
Total number of measurements						

Cleavage.—The cleavage common to the series, parallel to  $r'\{\bar{2}01\}$ , is very well developed in this salt. There is also a feeble and very imperfect cleavage parallel to  $b\{010\}$ ; it is not so distinct, however, as in several other ammonium salts of the series (ammonium magnesium, ammonium nickel, ammonium manganese, and ammonium copper sulphates).

#### Volume.

Relative Density.—Four determinations by the immersion method yielded the following values:—

· I.	Density f	for 18°·3/4°		2.2422	$\mathbf{For}$	$20^{\circ}/4^{\circ}$		2.2418
II.	,,	18°.7/4°		2.2445	,,	$20^{\circ}/4^{\circ}$		2.2442
III.	,,	18°·9/4°		2.2443	,,	20°/4°		2.2441
IV.	,,	18°.9/4°		2.2435	,,	20°/4°		2.2433
						Mean		2.2434

Accepted value for 20°/4°, 2.243.

The value 2.228 was obtained by Topsøe.

Molecular Volume. 
$$-\frac{M}{d} = \frac{485.68}{2.243} = 216.53.$$

Molecular Distance Ratios (topic axial ratios).—

$$\chi: \psi: \omega = 6.2520:8.4543:4.2678.$$

#### Optics.

Nature and Orientation of the Optical Ellipsoid.—The optic axes lie in the symmetry plane b {010}. The sign of the double refraction is positive. Extinction determinations with two section-plates ground parallel to the symmetry plane yielded the following results:—

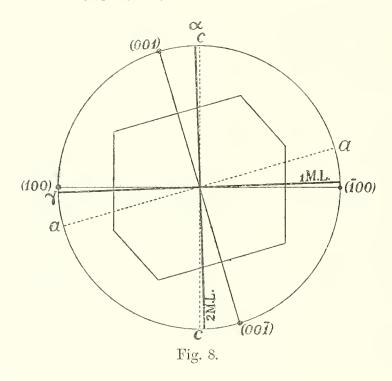
Extinction Direction in the Symmetry Plane.

Plate 1 . . . . 
$$14^{\circ} 18'$$
 Plate 2 . . . .  $14^{\circ} 16'$ , Mean . . .  $14^{\circ} 17'$ , behind the normal to  $c \{001\}$ .

This direction is the second median line, and corresponds to the refractive index  $\alpha$ , the other extinction direction at right angles in the symmetry plane being the first median line and corresponding to the index  $\gamma$ . As the morphological axial angle  $ac = 73^{\circ} 43'$ , and therefore the angle between the normal to  $c \{001\}$  and the vertical axis  $c = 16^{\circ} 17'$ , the second median line lies  $2^{\circ} 0'$  in front of the vertical axis c, in the obtuse angle ac of the morphological axes a and c. The first median line also lies in

the obtuse axial angle ac, 14° 17′ above the inclined axis a, and 2° 0′ below the normal to a {100}. These facts will be rendered clear by fig. 8.

Topsøe and Christiansen give the position of the first median line as 16° 54′ from the axis  $\alpha$  and 89° 25′ from the axis c.



Optic Axial Angle.—Three section-plates perpendicular to the first median line, numbered 1, 2, 3, and three others labelled 1a, 2a, and 3a, perpendicular to the second median line, were ground. The apparent optic axial angle in air, 2E, is too large for measurement, the brushes being not quite capable of being brought to the cross-wires; but excellent measurements were obtained for  $2H_a$  and  $2H_o$ , the apparent acute and obtuse angles in bromonaphthalene. The results, together with the values of the true optic axial angle  $2V_a$  calculated therefrom, are given in the accompanying table.

Ammonium Nickel Selenate.

Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$ .	No. of plate perp. 2 M.L.	Observed $2\mathrm{H}_{o}$ .	$egin{array}{c}  ext{Calculated} \  ilde{2} ext{V}_a. \end{array}$	$\begin{array}{c} \text{Mean} \\ 2 \text{V}_a. \end{array}$
Li	1 2 3	78 43 78 40 78 45	$ \begin{array}{c} 1a \\ 2a \\ 3a \end{array} $	85 8 85 2 85 6	86 18 86 20 86 20	86 19
C	$\frac{1}{2}$	78 41 78 38 78 43	1a 2a 3a	85 5 85 0 85 3	$   \begin{array}{c}     86 & 18 \\     86 & 20 \\     86 & 20   \end{array} $	86 19

DETERMINATION of True Optic Axial Angle in Bromonaphthalene (continued).	DETERMINATION	of True C	ptic Axial	Angle in	Bromonaphthalene	(continued).
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Light.	No. of plate perp. 1 M.L.	Observed $2H_a$ .	No. of plate perp. 2 M.L.	Observed $2H_o$ .	Calculated $2V_a$ .	Mean 2V <sub>a</sub> .
Na	1 2 3	78 21 78 21 78 22	1a $2a$ $3a$	84 40 84 41 84 39	$ \begin{array}{c}                                     $	86 21
т	1 2 3	78 2 78 5 78 5	1a 2a 3a	84 17 84 13 84 14	$   \begin{array}{c}     86 & 22 \\     86 & 25 \\     86 & 25   \end{array} $	86 24
Cd {	1 2 3	77 50 77 56 77 53	1a 2a 3a	84 3 83 57 83 54	$   \begin{array}{c}     86 & 22 \\     86 & 28 \\     86 & 28   \end{array} $	86 26
F	1 2 3	77 45 77 39 77 39	1a 2a 3a	83 45 83 38 83 35	$ \begin{array}{c} {}^{4}86 & 28 \\ 86 & 29 \\ 86 & 30 \end{array} $	86 29

Topsøe and Christiansen found 86° 14′ for  $2V_a$ .

Dispersion of the Median Lines.—Measurements with sections 1, 2, and 3 immersed in methyl salicylate, the refractive index of which (1.5363) is almost identical with the mean index of the crystals, indicated that the dispersion of the two mutually rectangular median lines lying in the symmetry plane is such, that the first median line lies nearer to the morphological axis a by about 12' for red C light than for greenish blue F light.

Refractive Indices.—Six 60°-prisms were prepared as usual, to afford two indices each,  $\alpha$  and  $\beta$ ,  $\beta$  and  $\gamma$ , or  $\alpha$  and  $\gamma$ , the bisecting plane being parallel to a principal plane, and the refractive edge parallel to one of the three principal axes, of the optical ellipsoid. The results are embodied in the accompanying table.

Refractive Indices of Ammonium Nickel Selenate.

Light.	α.	β.	γ.
Li	1.5246 $1.5251$ $1.5285$ $1.5320$ $1.5339$ $1.5360$ $1.5423$	1 · 5332 1 · 5337 1 · 5370 1 · 5405 1 · 5425 1 · 5447 1 · 5510	$ \begin{array}{r} 1 \cdot 5419 \\ 1 \cdot 5424 \\ 1 \cdot 5460 \\ 1 \cdot 5496 \\ 1 \cdot 5517 \\ 1 \cdot 5539 \\ 1 \cdot 5602 \end{array} $

Mean of  $\alpha$ ,  $\beta$ , and  $\gamma$  for Na light = 1.5372.

 $\alpha$  = Vibration direction parallel to second median line, 2° 0′ in front of vertical axis c.

 $\beta =$  ,, ,, ,, symmetry axis b.

 $\gamma =$  ,, ,, first median line, 14° 17′ above inclined axis a.

Double refraction,  $Na_{\gamma-\alpha} = 0.0175$ .

General formula for  $\beta$ , corrected to a vacuum:—

$$\beta = 1.5191 + \frac{690578}{\lambda^2} - \frac{1921310000000}{\lambda^4} + \dots$$

The  $\alpha$  indices are equally well reproduced by the formula if the constant 1.5191 is diminished by 0.0086, and the  $\gamma$  indices if it is increased by 0.0090.

Observations at 70° indicated that the refractive indices of ammonium nickel selenate diminish by about 0.0020 for a rise of temperature of 55°.

Axial Ratios of the Optical Ellipsoid.—The calculated values for the two types of ellipsoid are as under:—

Indicatrix . . . . . . . . .  $\alpha:\beta:\gamma=0.9945:1:1.0059$ . Optical Velocity Ellipsoid . .  $\mathfrak{a}:\mathfrak{b}:\mathfrak{c}=1.0055:1:0.9942$ .

Molecular Optical Constants.—These are given in the next table.

_	Axis of optical indicatrix	• •	α.	β.	γ.
LORENZ	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$ .	$\left\{ \begin{smallmatrix} C \\ G \end{smallmatrix} \right]$	$0.1366 \\ 0.1404$	$0.1385 \\ 0.1422$	$0.1404 \\ 0.1442$
,,	Molecular refraction, $\frac{n^2-1}{n^2+2}$ . $\frac{\mathrm{M}}{d}=\mathfrak{m}$	$\left\{ egin{array}{c} \mathbf{C} \\ \mathbf{G} \end{array} \right\}$	$66 \cdot 37$ $68 \cdot 18$	$ \begin{vmatrix} 67 \cdot 27 \\ 69 \cdot 08 \end{vmatrix} $	$68.19 \\ 70.03$
,,	Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$ Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$		$0.0038 \\ 1.81$	0·0037 1·81	0.0038 1.84
GLADSTONE	Molecular refraction, $\frac{n-1}{d}$ M	. С	113.70	115.56	117 · 45

Mean molecular refraction (GLADSTONE),  $\frac{1}{3}(\alpha + \beta + \gamma) = 115.57$ .

## Comparison of Results.

Habit.—The progression of habit which has been observed in all the other groups of double sulphates and double selenates of this large isomorphous series yet investigated (the work on the double sulphates having been completed by the author's last communication), is very clearly exhibited in this group of the double selenates containing nickel. The progression is characterised by the relative development of the faces of the forms c {001} and q {011}. In the potassium salt the basal plane c {001} is largely predominating, the faces of the clinodomal prism q {011} on each side of it being relatively small, as shown in fig. 1. In the cæsium salt, on the contrary, the two faces of q {011} predominate, and indeed confer a prismatic character on the crystal parallel to the inclined axis a, while the basal plane c {001} forms only a central strip, as exhibited in fig. 5. Distinctly intermediate between these two extreme types come the crystals of rubidium nickel selenate, in which the two forms are more nearly approached in relative size, the q {011} faces being larger

than in potassium nickel selenate but not so large as in cæsium nickel selenate. This will be clearly apparent from the typical crystal of the rubidium salt shown in fig. 3.

The ammonium salt forms crystals of all three types, but the great majority affect a more or less intermediate habit akin to that of the rubidium salt, while at the same time showing some idiosyncracies. Fig. 7 shows this well.

Crystal Elements and Angles.—The axial ratios and axial angles are compared in the following table. From an inspection of it the following facts become clear:—

Comparison of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
Potassium nickel selenate Rubidium ,, ,, Ammonium ,, ,, Cæsium ,, ,,	β. 104° 27′ 105° 20′ 106° 17′ 106° 11′	$a:b:c \ 0.7467:1:0.5059 \ 0.7395:1:0.5031 \ 0.7395:1:0.5048 \ 0.7288:1:0.4993$

The morphological axial angle of rubidium nickel selenate is approximately the mean of the axial angles of potassium nickel and cæsium nickel selenates, the differences being nearly identical, 53' and 51'. It will be remembered that the atomic weight of rubidium is almost exactly the mean of the atomic weights of potassium and cæsium. The axial angle of the ammonium salt is nearly identical with that of the cæsium salt. The morphological axial ratios of the rubidium salt are also intermediate between those for the potassium and cæsium salts. Hence, both axial angles and axial ratios for the three alkali metallic salts follow the order of the atomic weights of the alkali metals, and in the case of the axial angle with simple proportionality.

The axial ratios of the ammonium salt lie between those of the two extreme, the potassium and cæsium, salts, thus indicating true isomorphism of the ammonium salt with the alkali metallic salts.

The next table affords a comparison of the morphological angles of the four salts.

Comparison of the Interfacial Angles.

Angle.	KNi selenate.	RbNi selenate.	CsNi selenate.	AmNi selenate.		
$\begin{cases} ac &= (100) : (001) \\ as &= (100) : (101) \\ sc &= (101) : (001) \\ cr' &= (001) : (\bar{2}01) \\ cs' &= (001) : (\bar{1}01) \\ s'r' &= (\bar{1}01) : (\bar{2}01) \\ r'a &= (\bar{2}01) : (\bar{1}00) \end{cases}$	75 33	74 40	73 49	73 43		
	46 15	45 36	44 51	44 56		
	29 18	29 4	28 58	28 47		
	63 13	63 58	64 54	64 46		
	38 16	38 38 5	39 11	39 0		
	24 57	25 19 5	25 43	25 46		
	41 14	41 22	41 17	41 31		

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COMPARISON of the Interfacial Angles (continued).

Angle.	KNi selenate.	RbNi selenate.	CsNi selenate.	AmNi selenate.
$\begin{cases} ap &= (100): (110) \\ pp' &= (110): (120) \\ p'b &= (120): (010) \\ pb &= (110): (010) \end{cases}$	35 54 19 28 34 38 54 6	$35 \ 30.5$ $19 \ 28$ $35 \ 1.5$ $54 \ 29.5$	34 58 $19 28$ $35 34$ $55 2$	35 22 19 28 35 10 54 38
$\begin{cases} cq &= (001) : (011) \\ qb &= (011) : (010) \end{cases}$	26 6 63 54	$\begin{array}{ccc} 25 & 53 \\ 64 & 7 \end{array}$	$\begin{array}{ccc} 25 & 37 \\ 64 & 23 \end{array}$	25 51 64 9
$\begin{cases} ao &= (100): (111) \\ oq &= (111): (011) \\ aq &= (100): (011) \\ qo' &= (011): (\bar{1}11) \\ o'a &= (\bar{1}11): (\bar{1}00) \end{cases}$	49 30 27 33 77 3 34 26 68 31	48 49 27 25 76 14 34 50 68 56	$\begin{array}{cccc} 48 & 2 \\ 27 & 25 \\ 75 & 27 \\ 35 & 19 \\ 69 & 14 \\ \end{array}$	48 10 27 13 75 23 35 7 69 30
$\begin{cases} co &= (001): (111) \\ op &= (111): (110) \\ cp &= (001): (110) \\ po' &= (110): (11\bar{1}) \\ o'c &= (11\bar{1}): (00\bar{1}) \end{cases}$	78 20	34 40 42 54 77 34 57 34 44 52	$egin{array}{cccccccccccccccccccccccccccccccccccc$	$egin{array}{cccccccccccccccccccccccccccccccccccc$
$\begin{cases} bo = (010):(111) \\ os = (111):(101) \end{cases}$	$\begin{array}{cc} 69 & 56 \\ 20 & 4 \end{array}$	70 14 19 46	70 36 19 24	70 23 19 37
$\begin{cases} bo' = (010) : (\bar{1}11) \\ o's' = (\bar{1}11) : (\bar{1}01) \end{cases}$	65 10 24 50	65 12 24 48	65 19 24 41	65 2 24 58
$\begin{cases} sq &= (101) : (011) \\ qp &= (011) : (\bar{1}10) \\ ps &= (\bar{1}10) : (\bar{1}0\bar{1}) \end{cases}$	38 27 85 37 55 56	38 9 86 34 55 17	37 55 87 36 54 29	37 56 87 20 54 44
$\begin{cases} s'q &= (\bar{1}01) : (011) \\ qp &= (011) : (110) \\ ps' &= (110) : (10\bar{1}) \end{cases}$	45 10 63 55 70 <b>5</b> 5	45 21 63 26 71 13	$\begin{array}{c} 45 & 39 \\ 63 & 1 \\ 71 & 20 \end{array}$	45 37 62 44 71 39
$\begin{cases} r'o' = (\bar{2}01) : (\bar{1}11) \\ o'p = (\bar{1}11) : (110) \\ pr' = (110) : (20\bar{1}) \end{cases}$	34 38 92 54 52 28	$34  52 \\ 92  47 \cdot 5 \\ 52  20 \cdot 5$	35 4 92 57 51 59	35 16 92 22 52 22

These angles have all been carefully compared for the four salts and the differences tabulated, an analysis of the tables affording the following results. For thirty-five of the thirty-six angles compared the value for the rubidium salt is intermediate between the values for the potassium and cæsium salts.

The average and maximum changes of angle for the various replacements of one alkali base by another are given in the small table which follows, which forms an expressive summary of the tables of differences above referred to.

Angular	Changes	for	Double	Selenates	containing	Nickel.
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Replacement.	Average change.	Maximum change.
K by Rb	$\begin{array}{c} 7 \\ 23 \\ 47 \\ 45 \end{array}$	57 = 0 57 $119 = 1 59$ $110 = 1 50$

The average and maximum changes of angle are twice as great when potassium is replaced by cæsium as when potassium is replaced by rubidium, corresponding to the changes of atomic weight ( $K\sim Rb=46$  and  $K\sim Cs=93$ ). When potassium is replaced by ammonium the changes (average and maximum) are very nearly the same as occur when potassium is replaced by cæsium. That is to say, the average change in the crystal angles, and also the maximum amount of that change, in the cases of the metallic interchanges, are directly proportional to the change in the atomic weight of the alkali metal; while the introduction of the radicle ammonium instead of potassium produces about as much average or maximum change of angle as when potassium is replaced by cæsium, the actual amounts being very slightly less, to the extent of 2' in the average change (out of a total of 47') and 9' in the maximum change (out of a total of 1° 59').

From the above it will be clear that the differences in the crystal angles are of the same sign when potassium is replaced by rubidium on the one hand and by cæsium on the other, that is, there is a progressive change, there being only a single exception (in the case of an angle showing only a very small change) out of all the 36 cases compared; the amounts have been shown to be exactly proportional on the average to the two increments of atomic weight. In the case of the ammonium salt, 33 out of the 36 angles compared show differences on replacing potassium by ammonium in the same direction as when rubidium or cæsium are introduced instead of potassium, the only three exceptions being in cases where the differences are very minute. the 33 cases the changes are greater than when rubidium is introduced, and in 13 cases they exceed the effect produced by introducing cæsium for potassium. maximum change of angle for the ammonium replacement, however, has been shown to fall somewhat short of that for the cæsium replacement, and thus the crystal angles for the ammonium salt all fall within the limits of the changes for the three metallic salts, emphasising the true character of the isomorphism of all the four salts.

Volume Constants.—The densities, molecular volumes and topic axial ratios of the four salts are compared in the next table.

VOLUME Constants	of the	Nickel	Group of	Double	Selenates.
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Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios.
KNi selenate RbNi ,,	$527 \cdot 52$ $619 \cdot 62$ $713 \cdot 62$ $485 \cdot 68$	$2 \cdot 559$ $2 \cdot 856$ $3 \cdot 114$ $2 \cdot 243$	$206 \cdot 14$ $216 \cdot 96$ $229 \cdot 17$ $216 \cdot 53$	$\chi$ : $\psi$ : $\omega$ 6 · 1677 : 8 · 2598 : 4 · 1786 6 · 2533 : 8 · 4561 : 4 · 2542 6 · 3317 : 8 · 6878 : 4 · 3378 6 · 2520 : 8 · 4543 : 4 · 2678

The density increases with the atomic weight of the alkali metal, and is greater for the replacement of potassium by rubidium than for the replacement of rubidium by cæsium in the proportion of 6 to 5. The density of the ammonium salt is the lowest of the group, corresponding to the low molecular weight of the ammonium radicle NH<sub>4</sub>.

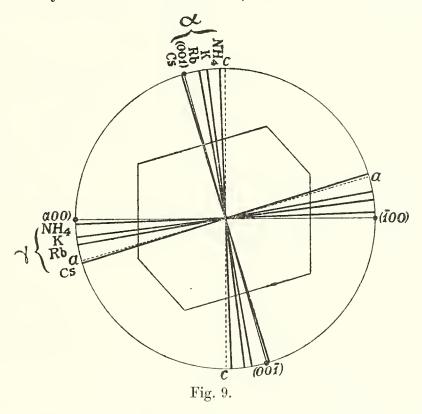
The molecular volumes of the three alkali-metallic salts show progression with the atomic weight of the alkali metal; the replacement of rubidium by existing is accompanied by the greater change, 12.21 units as against 10.82 units for the replacement of potassium by rubidium, so that the increment of volume is an increasing one. The molecular volume of the ammonium salt is almost identical with that of the rubidium salt, a result similar to what has been observed in all the other groups of salts of the series yet investigated.

The topic axial ratios of the rubidium salt are also intermediate between those for the potassium and cæsium salts, there being a regular progressive increase in the directional (axial-edge) dimensions of the structural unit cell of the space-lattice, when potassium is replaced by rubidium and the latter in turn by cæsium. The topic axial ratios of ammonium nickel selenate are almost identical with those of rubidium nickel selenate, the structural (space-lattice) unit cells of the rubidium and ammonium salts being thus almost identically congruent, that is similar in shape and symmetry and almost exactly equal in total volume and in the dimensions of their sides and edges. This result, similar to the results with all the other groups of double selenates yet investigated and of all the double sulphates and the simple alkali sulphates, thus forms yet another confirmation of one of the most remarkable facts brought to light by the author's investigations, namely, the extraordinary congruency of the ammonium and rubidium salts of any group; the replacement of two atoms of monad rubidium by eight atoms of monad hydrogen and two atoms of triad (at least, more probably pentad) nitrogen, actually occurs without any appreciable opening up of the structure. The bearing of this important fact on the theory of valency volumes of Barlow and Pope, with which it is in entire antagonism, is discussed in a separate communication (see Roy. Soc. Proc.).\*

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' A, vol. 93, p. 72 (1917).

Cleavage.—A cleavage parallel to the orthoprism  $r'\{\bar{2}01\}$  is well developed in the crystals of all four salts of the nickel double selenate group. In addition, the ammonium salt exhibits a feeble facility for cleavage parallel to the symmetry plane  $b\{010\}$ . This second direction of cleavage has also been observed more perfectly developed on the four double sulphates containing ammonium as the R-base and as M-metals, magnesium, nickel, manganese, and copper. It would appear to be connected with some obviously probable slight difference of structure, due to the different and more complicated chemical nature of the ammonium radicle NH<sub>4</sub> as compared with a simple alkali metallic atom. It is a fact which may prove later of value in elucidating the exact details of this slight difference of structure, and one which will require to be remembered in considering the meaning of the congruency with the rubidium salts referred to in the preceding paragraph.

Orientation of the Optical Ellipsoid.—This comparison is best effected by taking the position, in the crystals of the four salts, of that one of the two median lines



lying in the symmetry plane which is not far removed from the vertical morphological axis c, and which is the  $\alpha$  axis of the ellipsoid in all four salts. This principal axial direction of the optical ellipsoid is the second median line in all the salts but cæsium nickel selenate; in this latter salt it is by exception the first median line. Such a comparison is made in the following table, which is also illustrated by fig. 9.

Inclinations of a-Extinctions of the Ni Double Selenates in front of Axis c. (1M.L. in CsNi salt and 2M.L. in other three salts.)

AmNi selenate 2° 0′ RbNi selenate 9° 59′ KNi , 6° 59′ CsNi , 16° 51′.

The other principal axial direction of the ellipsoid lying in the symmetry plane shows, of course, a similar progression for the four salts, as it is always  $90^{\circ}$  from the direction compared in the table. The third rectangular axis of the ellipsoid is identical in position with the morphological symmetry axis b, and is, therefore, identical and immovable for all four salts, in accordance with monoclinic symmetry.

Thus the optical ellipsoid rotates about the symmetry axis when one alkali base is replaced by another. It is so situated in the ammonium salt that one axis is nearly identical with the vertical crystal axis c; it rotates from this position further away from c when ammonium is replaced by potassium, still further when the latter is replaced by rubidium, and yet further when rubidium is replaced by cæsium. Its position for the rubidium salt is thus intermediate between the positions for the potassium and cæsium salts, the rotations for the two replacements of K by Rb and Rb by Cs being respectively 3° 0′ and 6° 52′. The rotation is thus in the order of the atomic weights of the three alkali metals, the amount of the rotation increasing at a higher rate than in mere simple proportion to the change in atomic weight.

The Optic Axial Angles.—In making a comparison of these it has to be remembered that the first median line is differently situated in the cæsium salt; whereas for the potassium, rubidium and ammonium salts it is that principal axis of the optical ellipsoid lying near the inclined axis a, for the cæsium salt it is that axis of the ellipsoid which lies near the vertical axis c, the one 90° away near axis a being by exception in cæsium nickel selenate the second median line. We must, therefore, use the obtuse optic axial angle, the bisectrix of which lies near axis a and which is therefore comparable to the acute optic axial angles of the other three salts, the bisectrices of which lie also near axis a. With this understood, the following table affords the comparison.

OPTIC Axial Angles 2V<sub>a</sub> of the Nickel Group of Double Selenates.

	KNi selenate.	RbNi selenate.	AmNi selenate.	CsNi selenate.
Li	 7°2 4′5	8 <sup>2</sup> 2 2 <sup>3</sup> 3 .	86 19	97 19
C	 72 45	82 22	86 19	97 17
Na	 72 48	82 13	86 21	$96 \ 52$
Tl	 72 51	82 7	86 24	96 32
Cd	 $72 \ 53$	82 3	86 26	96 23
F	 $72 \ 56$	81 58	86 29	96 17

The optic axial angle is thus observed to increase with the rise in atomic weight of the alkali metal, the angle for the rubidium salt being intermediate between that for the potassium and cæsium salts, and the rate being again an accelerating one.

The optic axial angle of ammonium nickel selenate is slightly greater than that of the rubidium salt.

Comparison of the Refractive Indices.

Index.	Light,	KNi selenate	RbNi selenate.	$ m NH_4Ni$ selenate.	CsNi selenate.
α	Li	$1 \cdot 5142$ $1 \cdot 5147$ $1 \cdot 5181$ $1 \cdot 5212$ $1 \cdot 5232$ $1 \cdot 5251$ $1 \cdot 5314$	1.5161 $1.5166$ $1.5198$ $1.5231$ $1.5248$ $1.5268$ $1.5335$	1.5246 $1.5251$ $1.5285$ $1.5320$ $1.5339$ $1.5360$ $1.5423$	1.5358 $1.5363$ $1.5395$ $1.5428$ $1.5447$ $1.5467$ $1.5533$
$eta$ $\left\{ \left[ \right] \right.$	Li	1.5232 $1.5237$ $1.5272$ $1.5305$ $1.5325$ $1.5344$ $1.5407$	1.5253 $1.5258$ $1.5291$ $1.5325$ $1.5342$ $1.5362$ $1.5429$	1.5332 $1.5337$ $1.5370$ $1.5405$ $1.5425$ $1.5447$ $1.5510$	1.5412 $1.5417$ $1.5450$ $1.5483$ $1.5504$ $1.5525$ $1.5589$
$\gamma \ldots \left\{ \left[ \right] \right.$	Li	1.5387 $1.5392$ $1.5427$ $1.5464$ $1.5486$ $1.5507$ $1.5571$	1.5351 $1.5356$ $1.5390$ $1.5424$ $1.5443$ $1.5466$ $1.5534$	1.5419 $1.5424$ $1.5460$ $1.5496$ $1.5517$ $1.5539$ $1.5602$	1:5451 1:5456 1:5489 1:5526 1:5547 1:5568 1:5631
for Na light	index $\frac{1}{3}(\alpha + \beta + \gamma)$ n, $Na_{\gamma-\alpha}$	1.5293 $0.0246$	1 · 5293	1 · 5372 0 · 0175	1.5445

Refractive Indices.—The refractive indices are compared in the above table. It will be seen that the  $\alpha$  and  $\beta$  indices for the rubidium salt are intermediate between those of the potassium and cæsium salts. Owing, however, to the great diminution in double refraction  $(\gamma - \alpha)$ , which progressively diminishes as the atomic weight of the alkali metal present increases, the  $\gamma$  indices for the rubidium salt do not quite reach the value of these indices for the potassium salt. As another consequence of this the mean refractive index (mean of all three indices  $\alpha$ ,  $\beta$ ,  $\gamma$  for Na light) for the potassium and rubidium salts works out to be only just the same. As, however, the optical change is an accelerating one with the atomic weight of the alkali metal, in spite of the further diminution in double refraction when the cæsium salt is reached, all the indices (including the mean) for the cæsium salt show an advance.

The indices of the ammonium salt are intermediate between those of the rubidium and exsium salts.

The Double Refraction.—This is a property which shows the optical accelerating progression with the atomic weight of the alkali metal particularly well, as will be obvious from the values given at the foot of the table. Its effect is greater in this nickel group than in the magnesium and zinc groups already studied, in which groups the mean refractive index of the rubidium salt showed a considerable advance on that of the potassium salt.

#### AXIAL Ratios of the Optical Indicatrix.

					$\alpha$ : $\beta$ : $\gamma$	α	:	$\beta$	:	γ
KNi	selenate	٠		٠	0.9940:1:1.0101	0.9940	:	1	:	1.0101
RbNi	,,		•		0.9939:1:1.0065	0.9952	:	1.0012	:	1.0077
$\mathrm{NH_{4}Ni}$	"		•		0.9945:1:1.0059	1.0009	:	1.0064	:	1.0123
CsNi	23	٠	٠	•	0.9964:1:1.0025	1.0080	:	1.0116	•	1.0142

#### AXIAL Ratios of the Optical Velocity Ellipsoid.

					a : b :	¢	a	:	ъ	:	t
KNi	selenate			٠	1.0060:1:0	9900	1.0060	:	1	•	0.9900
RbNi	,,		٠	٠	1.0061:1:0.	9936	1.0049	:	0.9988	•	0.9923
$\mathrm{NH_4Ni}$		•			1.0055:1:0	9942	0.9991	:	0.9936	•	0.9878
CsNi	,,				1.0036:1:0	9975	0.9920	:	0.9885	:	0.9860

Axial Ratios of the Optical Ellipsoid.—The values of these ratios are given in the accompanying tables for both ellipsoids. The left hand series in each case are calculated with the  $\beta$  value for each salt taken as unity. The right hand series exhibit the total change in the dimensions of the optical ellipsoid on passing from one salt of the group to another, the  $\beta$  value for the initial potassium salt being taken as unity for all four salts. The main fact that these latter ratios indicate is the accelerating nature of the change in dimensions of the ellipsoid as the atomic weight of the alkali metal rises. The slight set-back of the  $\gamma$  values for the rubidium salt is due to the effect of the diminution in double refraction, as already explained. The dimensions of the ellipsoid of the ammonium salt are intermediate, another proof of the true character of the isomorphism, for they lie within the values for the extreme metallic salts of the eutropic series.

Molecular Optical Constants.—These are by far the most valuable of the optical constants, and they are set forth in order in the three next tables.

Table of Specific Refraction and Dispersion (Lorenz).

Salt.		Specifi	c refractio	on, $\frac{n^2 - 1}{(n^2 + 2)}$	$\overline{d} = \mathfrak{n}.$		Spec	eific disper	sion.	
	Fo	r ray C (H	[α).	For ray Hγ near G.			$\mathfrak{n}_{\scriptscriptstyle{\mathrm{G}}}-\mathfrak{n}_{\scriptscriptstyle{\mathrm{C}}}.$			
	α.	β.	γ.	α.	β.	γ.	α.	$\hat{eta}.$	γ.	
AmNi selenate KNi ,, RbNi ,, CsNi ,,	0·1366 0·1178 0·1059 0·1002	0·1385 0·1195 0·1074 0·1010	0.1404 $0.1225$ $0.1091$ $0.1016$	0·1404 0·1210 0·1088 0·1028	0.1422 $0.1227$ $0.1104$ $0.1037$	$\begin{array}{c} 0.1442 \\ 0.1258 \\ 0.1121 \\ 0.1043 \end{array}$	0·0038 0·0032 0·0029 0·00 <b>2</b> 6	0·0037 0·0032 0·0030 0·0027	0·0038 0·0033 0·0030 0·0027	

# Table of Molecular Refraction and Dispersion (Lorenz).

		Molecula	ır refractio	on, $\frac{n^2 - 1}{n^2 + 2}$ .	$\frac{M}{d} = m.$		Molec	cular dispe	ersion.		
Salt.	Fo	r ray C (H	[α).	For 1	For ray $H\gamma$ near $G$ .			$\mathrm{m_G}-\mathrm{m_C}$			
	α.	β.	γ.	α,	$\beta$ .	γ.	α.	β.	γ.		
KNi selenate RbNi ,, AmNi ,, CsNi ,,	$62 \cdot 14$ $65 \cdot 59$ $66 \cdot 37$ $71 \cdot 49$	$63 \cdot 04 \\ 66 \cdot 57 \\ 67 \cdot 27 \\ 72 \cdot 09$	64:60 67:61 68:19 72:52	63·82 67·39 68·18 73·37	64·75 68·38 69·08 73·98	66:37 69:47 70:03 74:44	1.68 1.80 1.81 1.88	1·71 1·81 1·81 1·89	1:77 1:86 1:84 1:92		

# Molecular Refraction (Gladstone and Dale).

Salt.		Mean molecular refraction for ray C.		
	$\alpha$ .	$\beta$ .	γ.	$\frac{1}{3}(\alpha+\beta+\gamma)$ .
KNi selenate	106·10 112·08 113·70 122·90	$107 \cdot 96$ $114 \cdot 07$ $115 \cdot 56$ $124 \cdot 14$	111·10 116·20 117·45 125·03	$108 \cdot 39$ $114 \cdot 12$ $115 \cdot 57$ $124 \cdot 02$

The whole of the specific and molecular optical constants of rubidium nickel selenate are intermediate between those of potassium nickel selenate and cæsium nickel selenate.

The molecular refraction increases considerably more when cæsium replaces rubidium than when the latter displaces potassium, the proportion being roughly as 5 to 3. The changes are nearly alike along the  $\alpha$  and  $\beta$  axis, but are less along the  $\gamma$  axis. These results are independent of the temperature, as both refractive power and density diminish (alter in the same direction) when the temperature is raised. The changes are obviously independent of the formulæ employed, for the results are similar whether the values compared are calculated by the formula of Lorenz or by that of Gladstone and Dale.

The position of ammonium nickel selenate with respect to molecular refraction is very close to that of the rubidium salt, in all cases less than one Lorenz or two Gladstone units higher. This result is very similar to that for the structural properties (dimensions), and again offers proof of the true isomorphism of the ammonium salt with the salts of the three alkali metals.

It is interesting to compare these results for the nickel double selenate group with those for the corresponding nickel double sulphate group. A comparison of the Lorenz and Gladstone values for the molecular refraction shows that the selenate values are higher by 6.9 to 8.1 Lorenz units, or 12.7 to 14.4 Gladstone units. As there are two atoms of sulphur or selenium present, this gives as the increase per atom, when sulphur is replaced by selenium, 3.5 to 4 Lorenz units or 6.3 to 7.2 Gladstone units. The following little table shows how these results for the replacement of sulphur by selenium in the nickel group compare with those obtained for the other groups already studied.

INCREASE of Molecular Volume on Replacing S by Se.

Ş	Salt	gr	oup	).			Lorenz units.	Gladstone units.
Nickel			٠		9		3.2-1.0	$6 \cdot 3 - 7 \cdot 2$
Magnesium							$3 \cdot 4 - 3 \cdot 6$ $3 \cdot 5 - 3 \cdot 7$	$6 \cdot 3 - 6 \cdot 7$ $6 \cdot 5 - 6 \cdot 9$
Zinc Simple salts							3 · 4 – 3 · 8	$\begin{array}{c} 6 \cdot 3 - 6 \cdot 9 \\ 6 \cdot 2 - 7 \cdot 2 \end{array}$

The values for the three groups of double salts are identical in the mean with those derived from the comparison of the simple rhombic alkali sulphates and selenates, which are therefore included in the table. This mean increase in molecular volume, when a sulphur atom is replaced by a selenium atom, in either series, is 3.6 Lorenz units, or 6.7 Gladstone units.

# Summary of Main Conclusions.

The results now presented for the nickel group of double selenates, of the monoclinic series  $R_2M\binom{S}{Se}O_4$ .  $6H_2O$ , are in line with those previously communicated for the

magnesium and zinc groups of double selenates, and for the eight groups of double sulphates, the investigation of which was completed by the publication of the author's last memoir (of June, 1915).\* The two main results are that the progression of all the morphological and optical properties of the crystals, with the atomic weight of the alkali metal (K = 38.85, Rb = 84.9, Cs = 131.9, and Rb-K = 46, Cs-Rb = 47), is beautifully shown once more in this nickel group of double selenates; and that the true isomorphism, but not eutropism, of the ammonium salt with the potassium, rubidium and cæsium salts is clearly indicated by the principal determinative constants (such as interfacial angles, size of the unit cell of the space-lattice, refractive indices and molecular refraction) of the ammonium salt never falling outside the limits of these constants for the two extreme, potassium and cæsium, salts of the group.

The former of these two main results is admirably illustrated by the fact that both the average and the maximum amounts of interfacial angular change, brought about by replacing one alkali metal by another, are directly proportional to the change in atomic weight. The differences of atomic weight between potassium and rubidium and between the latter and eximum are practically the same (46 and 47), and the changes in angle, whether the mean of all the changes of the 36 angles measured or the greatest change of angle observed, are also equal; or to express it differently, the replacement of K by Cs is accompanied by twice as much angular change as that of K by Rb (average changes K by Rb, 23', and K by Cs, 47', maxima 57' and 119'), just as the change of atomic weight Cs-K (= 93) is double that for Rb-K (= 46). The amounts are so large as to be entirely removed from any possibility of error, which, on a generous estimate, cannot exceed 3'.

The second main fact is illustrated by the closeness of the structural dimensions (those of the unit cell of the space-lattice) of the ammonium and rubidium salts, the rubidium salt being the intermediate metallic salt. So very close are the total volumes of the cells (the molecular volumes, for the Rb salt 216.96 and for the NH<sub>4</sub> salt 216.53) and their edge-lengths (the topic axial ratios), that the crystals of the two salts are practically iso-structural, that is, their space-lattices are congruent, practically identical, capable of being represented by the same model on any scale within reason.

The author has the more confidence in putting forward this important result inasmuch as the similar result found with regard to the simple rhombic alkali sulphates has just been verified in the laboratory of Prof. Bragg, by Prof. Ogg and Mr. F. Lloyd Hopwood,† who have succeeded in measuring the actual dimensions of the space-lattice cells (the distances separating analogous atoms of contiguous structural units in space) by means of the X-rays, these absolute lengths being in remarkable concordance with the author's published topic axial ratios. For this result, as to congruency of the ammonium and rubidium salts, has been general for

<sup>\* &#</sup>x27;Phil. Trans.,' A, vol. 216, p. 1 (1916).

<sup>† &#</sup>x27;Phil. Mag.,' November, 1916, vol. 32, p. 518.

all the rubidium and ammonium salts dealt with by the author, and it is most satisfactory to have it confirmed in such an incontrovertible and authoritative manner. Incidentally also, the value of molecular volume and of topic axial ratios, when used, as the author has always solely done, for the strictly comparable members of isomorphous series such as those now under discussion, is confirmed and enhanced.

The bearing of the very interesting work of Prof. Ogg and Mr. Hopwood on the theory of valency volumes is dealt with in a separate memoir.\*

#### [Added, February 7, 1917.]

With equal validity "atomic number" can be substituted for "atomic weight" in the statement of the author's law of progression of the crystallographic properties. For the differences between potassium, rubidium, and cæsium are similarly related as regards both functions, rubidium standing half-way between potassium and cæsium in both respects, as will be clear from the following comparison:—

		K.	Rb - K.	Rb.	$\mathrm{Cs}-\mathrm{Rb}.$	Cs.	Cs - K.
Atomic weights	٠	38.85	46	84.9	47	131.9	$93 = 2 \times 46.5$
Atomic numbers		19	18	37	18	55	$36 = 2 \times 18$

The differences between K and Rb, and Rb and Cs, are thus equal for both constants, namely, 46 or 47 in atomic weight and 18 in atomic number, and the difference between the two extreme members of the family group, potassium and cæsium, is double as much, namely, 93 for atomic weight and 36 for atomic number.

The atomic number, the sequence number of the element, when all the elements are arranged in order of ascending atomic weight in the periodic table, has acquired great significance from the work of Moseley, who in two memoirs on "The High Frequency Spectra of the Elements"† has shown definitely and experimentally that the atomic number represents the value of the charge N of positive electricity on the atomic nucleus. For we already knew from the work of Sir J. J. Thomson, Sir E. Rutherford, Barkla, van den Broek, and Bohr, sufficient concerning the structure of the atom to render it certain that there is an inner positively charged nucleus, surrounded by a number of negatively charged electrons approximately equal to half the atomic weight, and together equivalent electrically to the positive charge on the nucleus; and van den Broek and Bohr had suggested that the nuclear charge N would prove to be equal to the atomic number. Now N increases from the atom of one element to the atom of the next in the periodic table always by a

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' A, vol. 93, p. 72 (1917).

<sup>† &#</sup>x27;Phil. Mag.,' series 6, vol. 26, p. 1024 (1913), and vol. 27, p. 703 (1914); see also "Obituary Notice,' by Sir E. Rutherford, 'Roy. Soc. Proc.,' A, vol. 93, p. xxv. (1917).

single positive unit, the positive charge carried by the nucleus being in all cases an integral multiple of the charge on the hydrogen nucleus; thus, for instance, while hydrogen has one nuclear charge helium has two such charges, and lithium three. The decisive work of Moseley, in his latest (unhappily last) research,\* has been to show (a) that the X-ray spectra of the line series known as K are derived from the innermost ring of electrons, while those of the L series are derived from electrons further from the centre of the atom; (b) that the frequency of the spectra is proportional to  $(N-a)^2$  where a is a constant dependent on the line series used, its value being 1 for the K series and 7.4 for the L series (for the a line in each case); and a0 that N itself, the nuclear charge, is none other than the atomic number.

The atomic number, or element sequence number, is thus a very important factor in the constitution of the atom, and it is therefore very likely to be a correspondingly governing factor in determining the relative properties of an isomorphous series of salts, formed by the interchange of atoms of elements of the same family group of the periodic classification, such as the three alkali metals, which differ regularly from one another in position by two whole horizontal rows of elements at a time (18 elements). Indeed, the work of Moseley shows clearly that the properties of the atom are better defined by the atomic number than by the atomic weight. has always been difficult to see why mere atomic weight should wield the influence which has been pointed out by the author, and the author has been careful to emphasise that he regarded atomic weight as only another progressively changing property, very convenient, however, for purposes of reference as regards the chemical position of the element, but equally with all the other progressing properties dependent on some hitherto unknown fundamental difference in the chemical elementary atoms. This fundamental difference is now proved by Moseley to be the positive electric charge on the atomic nucleus, and as this determines the atomic electronic complexity and the atomic number is its measure, there is a logical reason why increase in the atomic number, in the case of a regularly ascending series of family group elements, should be effective in similarly progressively modifying the crystallographic and physical properties of isomorphous salts containing those elements. Moreover, the fact that both atomic weight and atomic number have been shown above to be similarly related, in the case of the alkali metals, rubidium standing exactly midway between potassium and cæsium in both respects, affords full explanation for the progression according to atomic weight which has been pointed out by the author to occur in the eutropically isomorphous series, both the rhombic simple salts and the monoclinic double salts, which have been described and compared in this and the author's former communications.

<sup>\* &#</sup>x27;Phil. Mag.,' series 6, vol. 26, p. 1024 (1913), and vol. 27, p. 703 (1914); see also "Obituary Notice," by Sir E. Rutherford, 'Roy. Soc. Proc.,' A, vol. 93, p. xxv. (1917).





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[PLATES 2 AND 3.]



# ON PHENOMENA RELATING TO THE SPECTRA OF HYDROGEN AND HELIUM.

 $\mathbf{BY}$ 

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Printers in Ordinary to His Majesty.

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By T. R. Merton, D.Sc. (Oxon), Lecturer in Spectroscopy, University of London, King's College, and J. W. Nicholson, M.A., D.Sc., Professor of Mathematics in the University of London.

#### Communicated by Prof. A. Fowler, F.R.S.

#### [Plates 2 and 3.]

#### Received June 16,—Read June 29, 1916.

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#### (I.) Introductory.

In recent years the spectra of Hydrogen and Helium have been perhaps more closely studied than those of any other element, owing partly to the importance of these substances in celestial bodies, and partly to the supposed simplicity of their atoms

which should render their spectra especially suited to theoretical investigation. Researches have been mainly directed to the study of the series relations in the spectra, and production of "enhanced" or "spark" lines under conditions of powerful excitation. The present investigation is devoted to a study of the spectra of Hydrogen and Helium, with special reference to the relative intensities of the lines under different conditions, a quantitative knowledge of which must necessarily be of importance in any discussion of the relation of spectra to the constitution of the atom.

It has been the custom to record the intensities of spectrum lines on an arbitrary scale, ranging generally from 10 for the strongest lines to 1 or 0 for the weakest. The intensities have usually been assigned purely at the discretion of the observer, and without much regard to the conditions of observation, whether visual or photographic. In any case, the apparent intensities are affected by the optical system by means of which the spectrum is produced, and whereas in visual observations the sensitiveness of the eye to different wave-lengths should be taken into account, matters are even more complicated in the case of photographs of spectra, where the sensibility of the photographic plate varies very considerably with the wave-length in a manner which is not precisely defined, and which appears in fact to be to a great extent irregular. These remarks apply to the visible and ultra-violet regions of the spectrum. Measurements in the infra-red are usually carried out with the thermopile or bolometer, and in this case quantitative measurements of the intensities of lines are obtained. It is, however, the visible and the less refrangible part of the ultra-violet spectrum in which accurate measurements of intensity, on a precise and quantitative basis, are perhaps most urgently needed at the present time. For example, in the case of celestial spectra, the problem of the relative intensities of lines has become of considerable importance, and is probably, at present, the greatest obstacle in the direction of the further elucidation of the phenomena which occur in new stars. In these spectra, observations are of necessity limited to the visible and the less refrangible ultra-violet regions.

The great advances which have been made already in the study of the variations in spectra under different conditions of excitation must owe their success largely to the magnitude of the effects in question; for they have depended to a great extent on methods of observation which cannot take account of the more subtle and less conspicuous variations which would probably, if detected, provide the key to the elucidation of many fundamental problems of spectra, such as the distribution of intensity in spectral series and the relations of different series to one another. At the present time, when a radiating gas emits a series spectrum, we have no exact knowledge of the relative amounts of energy thrown into the individual members of the series, or even whether these amounts are definite functions of the "term number," or capable of variation according to circumstances, although a certain amount of evidence has hitherto favoured the latter alternative.

#### (II.) Methods of Measurement.

For a number of reasons, measurements of the intensities of spectrum lines in the visible region with the thermopile or bolometer appear to be impracticable. In the first place, the intensity of the source must be exceedingly great if galvanometer deflections are to be obtained of a magnitude suitable for accurate measurement, and it is doubtful whether any but the brightest lines could be dealt with in this Moreover, it is only possible by such methods to deal with one line at a time, and the difficulty of maintaining sources of light constant for the duration of a series of measurements would, in many cases, appear to be almost insuperable. It would be necessary to introduce corrections for the loss of light in the spectroscope, and the determination of the magnitudes of these corrections would necessarily be a matter of considerable difficulty. Measurements have been made of the relative intensities of spectrum lines with the spectrophotometer. With this instrument it is difficult to attain any high degree of accuracy, and the range of wave-length over which it can be used is small unless the intrinsic intensity of the radiations is very great. It is, moreover, necessary to encounter the difficulty referred to above of maintaining the light source constant during a series of measurements.

In a recent paper,† we have discussed the application of a method, involving the use of a neutral-tinted wedge, to the determination of the distribution of intensity in broadened spectrum lines. In this case, the problem is reduced to its simplest form owing to the fact that over the short range of wave-length covered in a single broadened line, we may consider that both the extinction-coefficient of the wedge and the sensibility of the photographic plate remain constant. Such a method cannot be applied directly to the present problem without important modifications and additions, for in the measurement of the relative intensities of lines of widely different wave-length neither of these essential conditions is even approximately fulfilled, and, in addition, the loss of light in the spectroscope must be considered.

The problem dealt with in the present communication is therefore of an essentially different nature, but it has been found possible to evade these difficulties without altering the character of the method employed.

The apparatus used in the investigation is identical with that which we have described previously; and consists of a spectrograph, in front of the slit of which is mounted a neutral-tinted glass wedge, cemented to a similar wedge of colourless glass so as to form a plane-parallel plate. The spectra are photographed through the neutral wedge, and the resulting photographs consist of lines which are dark along the edge corresponding to the thin end of the wedge, and which fade away towards

<sup>\*</sup> Cf. Jolly ('Phil. Mag.,' xxvi., p. 801, 1913). A bibliography of the subject is given by this author and by Konen and Jungjohann ('Astrophys. Journ.,' xxxii., p. 141, 1910).

<sup>† &#</sup>x27;Phil. Trans.,' series A, vol. 216, p. 459.

<sup>‡</sup> Loc. cit,

the region corresponding to the dense end. Thus the lengths of the lines on the plate correspond to their intensities, and it is necessary in the first place to obtain accurate measurements of the lengths of all the lines under consideration. accomplished most conveniently by preparing positives from the negatives and enlarging the positives on to bromide paper through a ruled "process" screen. method provides an enlarged negative in which the lines are made up of minute dots, one hundredth of an inch apart, and the length of any line can be determined by pricking out the last visible dot, which is a perfectly definite and well-defined point, whereas in enlargements made without the "process" screen the determination of the "end of the line" is subject to a considerable amount of personal error. believe that with the use of the "process" screen, personal error is almost entirely We may now consider the method by which the lengths of the eliminated. photographed lines may be used in the determination of an actual relative intensity scale. As a preliminary, a precise knowledge of the constants relating to the wedge must be obtained.

# (III.) Determination of the Photographic Intensities of Lines.

The wedge employed was made of the so-called "neutral-glass" which shows no absorption of a selective character, but in which there is an increase of absorbing power with decreasing wave-length. If an incident intensity  $I_0$  falls on such a wedge at any point, and if I is the intensity transmitted, the *density* at that point is defined as the value of  $-\log_{10}(I/I_0)$ . The theory of the wedge is briefly as follows, and indicates the necessary account to be taken of the enlargement of the photographs, and the fact that the density so defined is the most convenient form of specification for future calculations.

If  $\rho_{\lambda}$  is the "coefficient of extinction" of the glass for light of wave-length  $\lambda$ , it is such that light of intensity  $I_1$ , falling on a thickness y of glass, is reduced during transmission to  $I_2$ , where

$$I_2 = I_1 e^{-y\rho_{\lambda}}$$

this law being equivalent to an exponential one. If  $\alpha$  is the angle of the wedge, and x the distance from the thin end,  $y = x \tan \alpha$  and the complete length of wedge being l, the intensity ratio for the complete wedge is

$$I_2/I_1 = e^{-\rho_{\lambda} l \tan a}$$

being the ratio of transmitted light at its ends, for the same incident intensity. The "density" is, therefore,  $-\log_{10} \left(I_2/I_1\right)$  or  $l \tan \alpha \cdot \rho_{\lambda}$  and will be denoted by  $D_{\lambda}$  for this particular wave-length.

If  $l_{\lambda}$  is the visible length of a line before enlargement, the visible length after enlargement is  $h_{\lambda}$  or  $l_{\lambda}H/l$ , where H is the length of the wedge after enlargement. For the magnification is equally  $h_{\lambda}/l_{\lambda}$  and H/l.

Let  $I_c$  be the intensity at which a line is just photographically visible. Then if its photographic intensity in the original light was  $I_{\lambda}$ , and if it is reduced to  $I_c$  by the thickness corresponding to a length  $l_{\lambda}$  of wedge, we have the relation

$$I_c/I_\lambda = 10^{-\rho_\lambda l_\lambda \tan \alpha}$$

or

$$\log_{10} (I_{\lambda}/I_{c}) = \rho_{\lambda}l_{\lambda} \tan \alpha = \rho_{\lambda}lh_{\lambda} \tan \alpha/H = D_{\lambda}h_{\lambda}/H$$

by the preceding relations, where  $D_{\lambda}$  is the density for this wave-length. Thus

$$\frac{I_{\lambda}}{I_{c}} = \log_{10}^{-1} \left( \frac{D_{\lambda} h_{\lambda}}{H} \right)$$

gives the photographic intensity of the original line, where  $D_{\lambda}$  is the density of the wedge, H the height of the wedge on the enlarged photographs, and  $h_{\lambda}$  the height of the line on the same photograph. The actual degree of enlargement adopted is immaterial, and so also, in the estimation of relative photographic intensities of different lines, is a knowledge of  $I_c$ , the intensity just visible photographically. We may, therefore, define the photographic intensity of a wave-length  $\lambda$  as

$$\log_{10}^{-1} \left( \frac{\mathrm{D}_{\lambda} h_{\lambda}}{\mathrm{H}} \right)$$

where the notation signifies an anti-logarithm, or the photographic intensities may be arranged on any arbitrary scale in which the ratios of this quantity are preserved. The subsequent reduction of photographic to absolute intensities will be considered in a later section.

## (IV.) The Density of the Wedge as a Function of Wave-length.

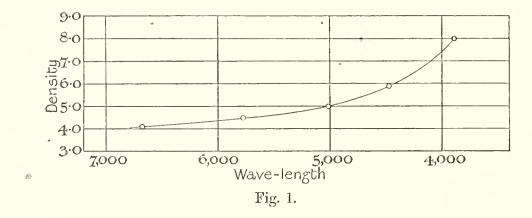
The density gradient of the wedge for different wave-lengths has been determined as follows:—As a primary standard of density we adopted two Nicol prisms, one of which could be rotated with respect to the other, the amount of rotation being read on a divided circle. These Nicol prisms were mounted in front of the slit of the spectrograph, the orientation of the fixed Nicol being such as to polarise the light in the same plane as the dispersing prism of the spectrograph. Light from a vacuum tube containing Helium passed through the two Nicol prisms and the neutral wedge, and an exposure was made for a definite time in the spectrograph, the movable Nicol being set in the same plane as the fixed Nicol. The gas in the vacuum tube was at a pressure estimated at about one millimetre of mercury, and was excited by means of an induction coil with a mercury break. For the comparatively short exposures which were involved, the light from this tube may be regarded as effectively constant. After the first exposure, a second exposure was made on an adjacent portion of the same plate and for the same time, the movable Nicol being now turned through the

appropriate angle to reduce the intensity of the light to one-tenth of its value in the previous exposure.

It is evident that the differences in the lengths of corresponding lines in the two exposures correspond to a reduction of intensity to one-tenth of its value, and are, therefore, the differences which would be produced by a step of density equal to 1.0 on the wedge for each of the various radiations measured. The calculation of the actual density of the wedge for each radiation then follows obvious lines. The following results were obtained for the wedge used in these experiments. Under  $\lambda$  are given the wave-lengths of the Helium lines which it was found convenient to use, and under  $D_{\lambda}$  the corresponding densities at the thick end of the wedge.

λ.	$D_{\lambda}$ .	λ.	$D_{\lambda}$ .
6678 5876 5015	$\begin{array}{c} 4 \cdot 1 \\ 4 \cdot 5 \\ 5 \cdot 0 \end{array}$	4471 3888 —	5·9 8·0

These values were plotted on squared paper, and from the curve thus obtained (fig. 1) which is quite regular, the density of the wedge for any intermediate wavelength can be found. There is no very convenient interpolation formula over the



entire region, although the first four values of  $D_{\lambda}$  are nearly in the inverse ratio of the wave-lengths. But the graphical method is sufficiently accurate.

## (V.) Determination of the Intensities of Lines in Terms of the Intensity of the Radiation from the Positive Crater of the Carbon Arc.

The reduction of photographic to absolute intensities implies the existence of a photographic record of some standard source of radiation extending over the whole region of wave-length examined. As a standard of radiation we have adopted the positive crater of the carbon arc burning in air at atmospheric pressure, and have

assumed that the distribution of energy in this source is that of a black body at the temperature of the boiling point of carbon. Assumptions involved in the use of this standard, and their general validity, will be discussed in a succeeding section.

The continuous radiation from the positive crater of the arc almost completely overpowers the band spectra which are superposed on it, except at certain regions in the spectrum where the intensities of the heads of bands cannot be neglected. But these regions, and points at which the lines due to impurities in the carbon are superposed, can easily be avoided in determining the photographic intensity curve of the arc. In Plate 2, A, is shown the photograph obtained of the spectrum of the positive crater of the carbon arc after the light had passed through the wedge. The Helium spectrum was superposed in order to provide lines of reference, and by measuring the height of the blackened area at a certain series of points, the photographic intensity curve of the positive crater has been determined. This curve refers, of course, only to the particular brand of plate employed, and must be re-determined for each batch of plates, or in the event of a particular batch being kept for a considerable time—for the sensibility curves of different batches may differ to some extent, and they are also subject to variation with time.

Plate 2, B, shows the Helium spectrum photographed through the wedge in the same manner, and, by measuring the heights of the lines, their relative intensities can be determined in terms of the intensity—for the same wave-length—of the carbon arc, by comparison with the photographic intensity curve of the positive crater. If, therefore, we can assume the distribution of absolute intensity in the continuous spectrum of the positive crater—corrected, of course, for the dispersion—we have the necessary data for determining the relative intensities of spectrum lines in absolute terms.

One of the main difficulties which at present somewhat restricts the accuracy which can be obtained by this method of comparison is our incomplete knowledge of the temperature of the crater. At the same time, very satisfactory results can be found from the existing data. The two temperatures usually quoted are T = 3700° C. absolute, found by Waidner and Burgess in 1904, and T = 3620° C. absolute, found by Harker in 1908, their mean being about 3650° C. absolute. These are blackbody temperatures of the positive crater. In connection with this question we have referred to Dr. J. A. Harker, F.R.S., of the National Physical Laboratory, who kindly informs us that the most probable temperature of the positive crater of the arc burning in air at atmospheric pressure should now be regarded as very close to 3750° C. absolute, or 100° C. higher than the mean. For purposes of comparison, we have, while accepting this estimate, computed according to both values in the following table.

Planck's formula for complete radiation is not necessary for the present values of wave-length and temperature, and Wien's law may be used. A measure of the intensity for a given wave-length  $\lambda$  is therefore  $\lambda^{-5}e^{-a\lambda/\tau}$  where  $\alpha = 1.445$  cm.

degrees. Thus, for the wave-length 6678, or  $6.678 \times 10^{-5}$  cms.,  $\alpha/\lambda\tau$  is equal to  $(1.445)10^{5}/(6.678 \times 3750)$  and is of order about 6.0. With wave-lengths in centimetres, and

$$I = \lambda^{-5} e^{-a/\lambda \tau}$$

the following results are obtained. The ratios exhibited are those for the given wave-length, with I for  $\lambda = 3888$  taken arbitrarily as unity.

CARBON	Arc with	Wien's	Law.

λ.	${f T}=rac{{f I}/{f I}_{3888}.}{3750.}$	${ m T/I_{3388}.} \ { m T}=3650.$	Percentage differences.
7065	4 · 347	4.910	12.9
6678	4.200	$4 \cdot 703$	12.0
5876	3.623	$3 \cdot 970$	9.6
5047	2.639	2.808	6 • 4
5015	2:595	2.758	6.1
4922	2.464	2.609	5.8
4713	2.148	$2 \cdot 253$	4 · 9
4472	1.810	1.8755	3.6
4438	1.761	1.821	3.4
4388	1.688	$1 \cdot 741$	3.1
4144	$1 \cdot 339$	$1 \cdot 362$	1.7
4121	1:308	$1 \cdot 328$	1.5
4026	1.178	$1 \cdot 189$	0.9
3965	1.098	$1 \cdot 104$	0.6
3889	1.000	1.000	0.0
3889	1.000	1.000	0.0

These percentage differences correspond to 100° C. As there is no reason to believe that the possible error in the temperature is of this magnitude, we may in any case adopt the values for 3750° C. with sufficient accuracy for the present purpose. These are the absolute relative intensities in the carbon are according to a certain scale.

Dispersion.—Uniformity of dispersion has been assumed in the calculation of these numbers. But the actual law of dispersion of the prism on the plates is approximately of the form

$$\lambda = \lambda_0 + \frac{\mathrm{B}}{x + x_0},$$

where x is the distance measured along the plate from a certain standard position,  $\lambda$ , B and  $x_0$  being constants. Thus

$$\delta \lambda = -B \, \delta x / (x + x_0)^2$$

and on the plate before enlargement an energy distribution of amount  $f(\lambda) d\lambda$  between wave-lengths  $\lambda$  and  $\lambda \times d\lambda$  is represented by the distribution of an amount

 $f(\lambda) \operatorname{B} dx/(x+x_0)^2$  within a distance dx centimetres, the apparent intensity at the point x being  $\operatorname{B} f(\lambda)/(x+x_0)^2$ . It is this law of intensity distribution on which the law of action of the wedge is actually superposed. The expression is equivalent to

$$f(\lambda)(\lambda-\lambda_0)^2/B$$

being the energy within a distance dx centimetres. After magnification m, this is spread over m dx centimetres, but as the magnification is the same for all regions of the spectrum, the intensity ratio on the plate for two wave-lengths  $\lambda_1$  and  $\lambda_2$  is

$$f(\lambda_1)(\lambda_1-\lambda_0)^2/f(\lambda_2)(\lambda_2-\lambda_0)^2$$

where both m and B disappear. The true relative intensities of the carbon arc at  $\lambda_1$  and  $\lambda_2$  affecting the plate are, therefore, obtained by multiplying the entries in the preceding table for  $\lambda = \lambda_1$  and  $\lambda = \lambda_2$ . T = 3750° C. absolute, respectively by  $(\lambda_1 - \lambda_0)^2$  and  $(\lambda_2 - \lambda_0)^2$ .

The actual approximate law of dispersion for the plate used in the case of the carbon are was

$$\lambda = 2257.5 + \frac{116802.9}{x + x_0}$$

so that  $\lambda_0 = 2257.5$ . But for  $\lambda$  close to  $\lambda_0$ , a better approximation is obtained by direct comparison of a prepared wave-length scale, which fits the lines, with an ordinary millimetre scale.

Again taking  $\lambda 3888$  as the standard of reference, the following table has been constructed for the absolute relative intensities in the arc with which the individual lines in the Helium spectrum must be compared:—

Table of Absolute Relative Intensities (Energy Densities) of Carbon Arc on the Plate.

	λ.	Ratio to λ3888 (Wien's law).	Ratio corrected for dispersion.	λ.	Ratio to \$3888 (Wien's law).	Ratio corrected for dispersion.
20	7065 6678 5876 5047 5015	$\begin{array}{c} 4 \cdot 347 \\ 4 \cdot 200 \\ 3 \cdot 623 \\ 2 \cdot 639 \\ 2 \cdot 595 \end{array}$	$   \begin{array}{r}     28 \cdot 98 \\     28 \cdot 00 \\     16 \cdot 10 \\     7 \cdot 04 \\     6 \cdot 92   \end{array} $	4472 4438 4388 4144 4121	1·810 1·761 1·688 1·339 1·308	$   \begin{array}{r}     3 \cdot 02 \\     2 \cdot 73 \\     2 \cdot 56 \\     1 \cdot 73 \\     1 \cdot 61   \end{array} $
	$\frac{4922}{4713}$	$2 \cdot 464 \\ 2 \cdot 148$	6·08 4·475	402 <b>6</b> 3965	1·178 1·098	1 · 31 1 · 17

It is evident that no correction for dispersion is required in the case of individual lines in a series spectrum, the preceding investigation being only necessary in the case of continuous spectra. For the energy in the line spectrum is confined to narrow

regions of wave-length, and does not require expression as an energy density per unit length. The effect of unequal dispersion in any narrow region is negligible. If, however, the line were very broad, dispersion would become important within its extent, as in the case of  $H_a$  under the conditions of excitation employed in the work described in the preceding communication.\*

When the wave-length scale is used, it is only necessary to multiply the theoretical ratio in the second column by  $\frac{d\lambda}{dx} / (\frac{d\lambda}{dx})_{3888}$ , which can be read directly.

## (VI.) The Energy in an Emission Line.

In the case of emission lines, the intensities to which we have referred hitherto in this communication have been "central intensities," or the maxima of energy density in the lines. The central intensity determines the height of the line when it is photographed through the wedge, and "photographic intensity" has signified photographic central intensity. But every line, however narrow, has a definite breadth within which dispersion, for lines so narrow as those dealt with in the present experiments, may be regarded as uniform. If all lines were equally sharp, it is evident that this central intensity would be a satisfactory measure of the actual energy-content of the line, but the condition of equal and extreme sharpness cannot be assumed to occur, except under certain specified circumstances.

If  $I_c$  is the intensity just visible photographically, the height of the line, originally of intensity  $I_{\lambda}$  at its centre, on the plate after enlargement is, with the previous notation,  $h_{\lambda}$ , where

$$\frac{I_{\lambda}}{I_{c}} = \log_{10}^{-1} \left( \frac{D_{\lambda} h_{\lambda}}{H} \right) = 10^{\frac{D_{\lambda} h_{\lambda}}{H}}$$

and  $I_{\lambda}/I_c$  is the quantity defined already as the photographic intensity, representing actually the photographic central intensity. The critical intensity  $I_c$  affecting the plate is a function of  $\lambda$ , so that the use of the carbon arc is necessary as a standard of comparison, but in an individual line,  $I_c$  may be treated as constant, together with  $D_{\lambda}$ .

Taking account of both sides of the line, the whole energy in it is proportional to

$$2\int I_{\lambda} d\lambda = 2I_{c} \int 10^{\frac{D_{\lambda}h_{\lambda}}{H}} d\lambda$$

where the upper limit is effectively infinite, and the lower one is the wave-length of the central component. The law of energy distribution in the line determines the dependence of  $h_{\lambda}$  on the wave-length. There are two important cases:—

(1) The law of the simple exponential, found in the former paper\* to be applicable in the case of the condensed discharge; and

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(2) The probability law, valid for the ordinary discharge. If we take first the simple exponential, then before incidence on the wedge, if I is the intensity of the central component at  $\lambda = \lambda_1$ ,

 $I_{\lambda}/I = e^{-k(\lambda - \lambda_1)},$ 

and after incidence, the trace on the final plate is a straight line on either side of the central component of height  $h_{\lambda_i}$ . The height at wave-length  $\lambda$  is

$$h_{\lambda} = h_{\lambda_1} \left( 1 - \frac{\lambda - \lambda_1}{b} \right)$$

from the equation to the straight line, where B is the half breadth on the photograph. Substituting this value in the integral, the total energy becomes

$$2\mathrm{I}_{c}\,10^{(\mathrm{D}_{\lambda}h_{\lambda_{\mathrm{I}}}/\mathrm{H})}\!\int_{\lambda_{\mathrm{I}}}^{\infty}\!d\lambda\,\,.\,10^{-\mathrm{D}_{\lambda}h_{\lambda_{\mathrm{I}}}(\lambda-\lambda_{\mathrm{I}})/\hbar\hbar} = \frac{2\mathrm{I}_{c}b\mathrm{H}}{\mathrm{D}_{\lambda}h_{\lambda_{\mathrm{I}}}\log_{e}^{10}}\,\,.\,10^{(\mathrm{D}_{\lambda}h_{\lambda_{\mathrm{I}}})/\mathrm{H}}\,,$$

and is therefore proportional to

where the breadth of the line on the base of the wedge photograph is implied, and the photographic intensity is that of the central component. It is not difficult to prove in a similar manner that when the law of distribution in a line of the original light is that of probability, the whole energy in a line is proportional to the quantity

(breadth) (photo. intensity)/
$$\sqrt{\log \text{ (photo. intensity)}}$$

with the same definitions of breadth and intensity as determined from the wedge photograph. It is therefore necessary, in obtaining absolute measures of contained energy, for comparison along a given spectrum series, to consider the circumstances of production of the lines; but these two cases include those which have at present been explicitly recognised, and the effective one can at once be seen by inspection of the photographs.

The dispersion used in the present experiments has, in most cases, not been sufficient to overcome the effects of irradiation, which must be reduced to a relatively small magnitude in order to determine the true breadth of a line, which is small, at the base of the wedge photograph. The quantitative information contained in this portion of the paper is, therefore, limited to the maximum intensities of the lines, which provide a basis at present sufficient to elucidate the main phenomena, and from which the absolute ratio of the energy contents can be determined at any subsequent time by measurements of the relative breadths of the lines concerned, with a high dispersion, and without the necessity of repeating the present measurements. But it is important to notice that the use of the ruled "process" screen supplies a very

accurate method of determining the breadths, which is of much greater value than any method of direct measurement. For the measurement of such small distances cannot achieve a high degree of accuracy, even with the aid of a construction on the plate, giving a geometrical magnification.

According to the conditions of discharge, the bounding curves on the plate are either straight lines or parabolas, and in both cases the breadths at the base can be determined as follows:—The dots on the photographs produced with the screen are at the rate of 100 to the inch—in order of magnitude—in two perpendicular directions. They are so close that the area of any blackened region is very accurately proportional to the number of contained dots. Under a magnifying lens, these dots can be counted visually without difficulty, and the breadth of the line is proportional to the number of dots divided by the height. The preceding formulæ for the absolute contained energy could therefore be put into the form:—

(Number of dots) (photo. intensity)/(height) (log<sub>10</sub> photo. intensity)<sup>n</sup>

where  $n = \frac{1}{2}$  for the ordinary discharges, and n = 1 for the condensed discharge. Even in the case of parabolas, the area is a definite numerical fraction of that of the containing rectangle.

The photographic intensity measures and the dot counts need not be done simultaneously on plates of the same magnification—the degree of magnification is not relevant to the formula—as is readily perceived, though, of course, the enlargements should be made from the same negatives.

The breadth of a line, of course, requires correction by the dispersion factor  $(\lambda - \lambda_0)^2$ , where  $\lambda_0 = 2257.5$  in these experiments, regarded as uniform across the line, and must be multiplied for each line by this factor. The effect of enlargement does not enter directly at this point into the question of integrating the whole energies in the lines, for it acts equally on all the lines. The energy is proportional to  $I_c$  which must be eliminated by comparison with the carbon arc.

We may, for purposes of clearness, summarise the results of this section and of the preceding sections in the following terms:—

In the quantitative analysis of a spectrum line by comparison with the carbon are regarded as giving black-body radiation, there are two important magnitudes to be considered:—(1) the maximum energy-density at the centre of the line, I, such that the energy distribution in the line at its centre is  $I_{\lambda} d\lambda$  for a small range  $d\lambda$  of its width, and (2) the whole energy-content of the line, or the energy thrown into this wave-length when the gas is emitting its series spectrum. In the case of the carbon are emitting a continuous spectrum, we only have energy-density to consider, and it can furnish a standard of comparison for both (1) and (2). The absolute relative intensities of the carbon are for any wave-lengths can be calculated theoretically, and are exhibited in a previous table in the preceding section. Their photographic

effect as affected by the wedge can be thrown on the same plate with a series spectrum under the same conditions.

In order to determine from this plate the relative maxima of energy-density, or the relative central intensities of the lines in the series spectrum, as in (1), we apply the formula

(photo. intensity of line) (absolute intensity of arc)/(photo. intensity of arc)

for each wave-length. The dispersion factor enters into the absolute intensity of the arc, but into neither of the other quantities concerned. The relative central intensities are proportional to the results thus calculated.

But in order to determine the relative energy-contents of the lines, as in (2), we must use the formula, where  $n = \frac{1}{2}$  or 1,

(breadth of line) (photo. intensity of line) (absolute intensity of arc) (photo. intensity of arc) (log of photo. intensity of line)<sup>n</sup>

which is the formula already deduced in this section, with the variable  $I_c$  removed by substitution of absolute intensity divided by photographic intensity in the arc, to which it is proportional. The dispersion ratio automatically cancels from the formula in this second case, as in fact it should in the present method whenever two magnitudes at the same wave-length, which involve a consideration of a range  $d\lambda$  in the neighbourhood of this wave-length, are to be compared.

## ✓ (VII.) The Helium Spectrum under Different Conditions.

One of the most interesting applications of the preceding theory does not involve the carbon arc, and consists of the examination of the relative behaviour of Helium lines under different conditions of excitation. In this case, we are not concerned with the intensity of one line in a spectrum relatively to the others, but with the changes of intensity of one line under different conditions relatively to those in other lines under the same conditions. Some interesting results in this connection have been obtained, and it is perhaps convenient to give some account of them before proceeding to the comparative intensities along the whole spectrum at any one time. The dispersion does not enter into the question in this case, when the lines are produced in the same manner on the same plate, and the ratio of the central intensities of any line from the two sources is the ratio of the photographic intensities which it shows, the photographic intensity being again  $\log_{10}^{-1} \left(\frac{D_{\lambda}h_{\lambda}}{H}\right)$ , where  $h_{\lambda}$  is the height of the line,  $D_{\lambda}$  the density of the wedge at the particular wave-length, and H the height of the wedge on the enlarged photograph.

In the following table are exhibited the results and intermediate steps in one important case—the ordinary Helium spectrum and the spectrum as given by the bulb. In each case, H was equal to 34.0 mm.

By "ordinary" Helium spectrum is meant the spectrum given by the capillary of a vacuum tube containing Helium at a pressure of about one millimetre, and excited by the discharge from an induction coil without capacity or a spark-gap. The bulb discharge was obtained by putting a small condenser in parallel with a very small spark-gap in the circuit. The intensity of the condensed discharge was not sufficiently great to give rise to any appreciable broadening of the lines. This observation was made by means of a Fabry and Perot interferometer. It must be pointed out that no attempt has been made to compare the intrinsic brightness of the lines under different conditions. The intensities given refer to an arbitrary unit, and the measurements refer to the relative intensities on the photograph. It is, therefore, the ratios of the intensities under different conditions, for the various lines, and not the intensities themselves from which conclusions may be drawn.

	$D_{\lambda}$ .	Helium (ordinary).			Helium (bulb).			
λ.		$h_{\lambda}$ .	$h_{\lambda}^{\bullet}D_{\lambda}/H.$	Photo- graphic intensity.	λ.	$h_{\lambda}D_{\lambda}/H$ .	Photo- graphic intensity.	Ratio.
7065	3.95	9.5	1 · 104	12.7	2.0	0.232	1.71	0.133
6678	4.1	$17 \cdot 2$	$2 \cdot 074$	118.6	$12 \cdot 5$	1.507	32.1	0.27
5876	4.5	18.8	2.489	308	$17 \cdot 4$	2.303	201	0.65
5047	5.0	4.0	0.589	3.88		0		
5015 -	5.0	12.5	1.838	68.9	$8 \cdot 9$	1:309	20.4	0.29
4922	5.15	$9 \cdot 2$	$1 \cdot 394$	$24 \cdot 8$	8.9	1.348	$22 \cdot 3$	0.900
4713 .	5.45	12.8	$2 \cdot 052$	113	10.4	1 · 667	46.5	0.41:
4472	5.9	14.8	2.568	370	$17 \cdot 8$	3.089	1227	$3 \cdot 32$
4438	6.0	3.0	0.530	3.39	$6 \cdot 4$	1.130	13.5	$3 \cdot 98$
4388	6.13	6.8	$1 \cdot 226$	16.8	$7 \cdot 7$	1.388	$24 \cdot 4$	1.46
4144	6.9	$2 \cdot 2$	0.447	$2 \cdot 80$	$3 \cdot 4$	0.690	$4 \cdot 90$	1.75
4121	$6 \cdot 95$	$5 \cdot 0$	1.022	10.5	$4 \cdot 8$	0.981	9.57	0.91
4026	7 · 4	6.0	1:306	$20 \cdot 2$	$7 \cdot 9$	1.720	52.5	2.60
3965	7 · 7	$3 \cdot 6$	0.815	6.53	3.6	0.815	6.53	1.00
3888	8.0	$8 \cdot 7$	$2 \cdot 047$	111.4	6.0	1:412	25.8	0.23

The ratio in the last column is the intensity in the bulb divided by that with the ordinary discharge, and the series of values is very remarkable. Certain lines are, in the bulb, centrally enhanced to a great degree at the expense of others, and since experiments with the interferometer show that the widths of the lines are not sensibly different under these conditions, the results cannot be explained on the assumption that they are broader in one case and, therefore, for a given energy-content, less intense centrally. There is an actual preferential emission of energy which is essentially different in the two sources.

It is instructive to examine these ratios in the light of the known series relations between the lines. The Diffuse series of Helium contains the lines  $\lambda\lambda 5876$ , 4471, 4026, whose "term numbers" are m=3,4,5. In the bulb, the first is reduced to  $\frac{2}{3}$  its former central intensity, the second is increased in the ratio  $3\frac{1}{3}$ , and the third

in the ratio  $2\frac{1}{2}$ . This appears to imply that in the bulb, a definite transfer of the energy of emission takes place towards the lines of higher term number—mainly in the present circumstances from the first to the second, but quite definitely also towards the third. If this be the correct interpretation, it has an obvious bearing on the anomalies met with in the spectra of nebulæ, where  $\lambda\lambda 4472$  and 4026, with  $\lambda 4388$  and, to a less extent,  $\lambda 4143$  are abnormally bright in many cases in comparison with such lines as D<sub>3</sub>. Examination of the other lines only serves to indicate the generality of this interpretation. The Sharp series of Helium contains, as its leading members,  $\lambda\lambda7065$ , 4713, 4121, corresponding to m=3,4,5. Instead of the actual enhancement found in the later members of the Diffuse series, these are all reduced in the bulb, so that there is relatively less radiation sent out in the form of the Sharp series. But the nature of the reduction is very significant. For  $\lambda 7065$  is reduced to about  $\frac{1}{10}$ ,  $\lambda 4713$  only to  $\frac{4}{10}$ , and  $\lambda 4121$  only to  $\frac{9}{10}$ , so that the preferential transfer of the Sharp series energy is perhaps even more pronounced than that of the Diffuse series. The only line of the Principal series in the region we have examined is λ3888, so that no conclusions can be drawn regarding it.

The Diffuse series of Parhelium contains  $\lambda\lambda6678$ , 4388, 4144, corresponding to  $m=3,\,4,\,5,\,6$  in the formula. This series exhibits the same phenomenon in a very pronounced manner. For in the bulb spectrum  $\lambda6678$  is reduced to  $\frac{1}{4}$ , but  $\lambda4922$  only to  $\frac{9}{10}$ , while the next member,  $\lambda4388$ , is actually enhanced to  $1\frac{1}{2}$ , and the next,  $\lambda4144$ , is even further enhanced to  $1\frac{3}{4}$ . These are the other two lines mentioned already in connection with their enhancement in nebulæ.

An even more striking fact in the same connection occurs with the Sharp series of Parhelium. Its first visible member appears in our ordinary Helium spectrum, but is quite invisible in the wedge photograph from the bulb. This is the line  $\lambda 5047$ . But the next member,  $\lambda 4437$ , is visible in both, and is enhanced in the ratio 4.0 in the bulb. The next member, λ4169, is visible in the ordinary spectrum of the bulb, though not in the wedge photograph, and is quite invisible with the ordinary discharge for the exposure given, even without the interposition of the wedge. This is a significant illustration of the effectiveness of the wedge method for determining variations incapable of detection by visual methods. The absence of this line in the ordinary spectrum, and its presence in the bulb under the same conditions, might have been noticed by visual or ordinary photographic methods. But without the present method of detecting comparatively small differences in order of intensity as estimated by ordinary and very unsensitive methods—it would have been impossible to interpret this phenomenon as part of a general effect extending throughout the spectrum, and an effect which must be fundamental to any theory of the origin of spectra.

There remains the Principal series of Parhelium, whose members in the range examined are  $\lambda\lambda 5015$  and 3965. The same phenomenon is shown, for the former is reduced in the bulb to  $\frac{3}{10}$ , and the latter has the same intensity in both cases.

It is, therefore, a general fact that, without exception, the energy in the bulb spectrum has been transferred towards the members of higher term number in all the component series—provided, as later investigation shows, that the effect is not due to a mere change in the energy distribution within the lines.

The Helium Spectrum from the Capillary with a Condensed Discharge.—
On Plate 3 is shown the wedge photograph of the Helium spectrum from the capillary produced by means of a powerful condensed discharge with a spark-gap in the circuit, and for comparison, the ordinary spectrum developed on the same plate. The quantitative analysis follows the same method as in the last section, and the results for one plate are exhibited in the table below. On this particular enlargement the full length of the wedge was 35 mm.

			Не	Helium ordinary).			Helium (condensed discharge).		
	λ.	$D_{\lambda}$ .	$h_{\lambda}$ .	$h_{\lambda} D_{\lambda} / H.$	Photographic intensity.	$h_{\lambda^*}$	$h_{\lambda} D_{\lambda} / H.$	Photographic intensity.	Ratio cond./ord.
	7065	3.95	3.7	0.418	2.62	_	_	_	_
	6678	4.1	$12 \cdot 3$	1.441	27:61	13.8	1.617	41.4	1.50
	5876	4.2	$18 \cdot 2$	2.340	219	$18 \cdot 2$	2.340	219	1.00
	5047	1 2.0	_	_		_	_	_	
	5015	2.0	11.5	1.643	44.0	10.0	1.428	26.8	0.596
	4922	5.12	$7 \cdot 0$	1.030	10.7	$7 \cdot 9$	1:162	14.5	1:355
	4713	5 · 45	10.2	1.588	$38 \cdot 7$	10.7	1.666	46.3	1:20
7	4472	5.9	15.7	2.647	111	$15 \cdot 7$	2:647	444	1.00
	4438	6.0				1.8	0:309	2.04	
	4388	6.13	$5 \cdot 1$	0.893	7.82	$7 \cdot 7$	1.343	22.0	$2 \cdot 82$
	4144	6.9		_		1.5	0.296	1.98	
	4121	6.95	$2 \cdot 5$	0.496	3.13	$4 \cdot 0$	0.794	6.22	1.99
	4026	7.4	6.0	1 · 269	18.6	6.0	1.269	18.6	1.00
	3965	$7 \cdot 7$	3.5	0.770	5.89	$3 \cdot 9$	0.858	$7 \cdot 21$	$1 \cdot 225$
	3888	8.0	9 · 1	2.080	120	8.5	1.943	.87 · 7	0.729

The most significant feature of these results is the fact that the central intensities for the three lines of the Diffuse series of Helium are the same on both photographs. When their heights were found to be the same in both cases, they were re-examined, and no difference can be detected. The fact that their "absolute" heights were identical was of course accidental. At the same time the shapes of the lines are quite different (Plate 3), for  $\lambda 4472$  is very much broader, and therefore contains, for the same height, very much more energy. The same applies to  $\lambda 4026$ , and to a less extent to  $\lambda 5876$ , but the increase in  $\lambda 5876$  is not comparable with that in  $\lambda 4472$  or even  $\lambda 4026$ . We are in the presence of the same phenomenon as before, but with the difference, that whereas in the bulb the transfer to higher members of the series takes the form of increased central intensity but not increase of breadth, with the condensed discharge the extra energy goes into the form of increased breadth.

The Sharp series of Helium,  $\lambda\lambda7065$ , 4713, 4121 exhibits the transfer in a more normal manner. As regards central intensity alone,  $\lambda7065$ , while giving a definite trace on the wedge photograph in the ordinary spectrum, cannot be detected on the corresponding photograph with the condensed discharge.  $\lambda4713$  is enhanced in the ratio 1'20, and  $\lambda4121$  in the ratio 1'99, which is much greater. At the same time, each of these two lines is considerably broader, so that the enhancement of their energy-content is very great. The Principal line  $\lambda3888$  is slightly broadened by the condensed discharge, and its central intensity is reduced to 0'7. Again no conclusion can be drawn without another line for comparison.

The Diffuse Parhelium series,  $\lambda\lambda6678$ , 4922, 4388 is enhanced in the ratios 1.50, 1.355, 2.82. Both the Diffuse series are relatively enhanced with the condensed discharge. The lines become progressively broader towards the violet, so that the energy-enhancement of  $\lambda4388$  is very great in comparison with that of  $\lambda6678$ , and that of  $\lambda4922$  exceeds that of  $\lambda6678$  when its breadth is taken into account.

In connection with the nebular spectrum, it is interesting to notice that  $\lambda\lambda 4472$ , 4388, 4026 are enhanced by the condensed discharge to an abnormal extent in comparison with any other lines, and their increase of breadth makes the effect more conspicuous.

The Sharp series of Parhelium is normal, for  $\lambda 5047$  is not visible through the wedge in either case, and  $\lambda 4437$  only with the condensed discharge. For the Principal series,  $\lambda 5015$  is reduced to  $\frac{6}{10}$ , whereas  $\lambda 3965$  is enhanced to  $\frac{11}{9}$ ,—again a normal effect. The broadening with decreasing wave-length is, although definite, much less striking in these series, and its most pronounced effects occur in the two Diffuse series.

The transference of energy of emission to the higher members of the series is actually much greater with the condensed discharge than in the bulb, although it is not so strikingly apparent owing to the broadening of the Diffuse series, which are the most affected.

The fundamental importance of a phenomenon of this type is perhaps a sufficient justification for exhibiting the results derived from a third plate—in which all the three spectra are present together. The height of the wedge in the enlargement is 34 mm. for the condensed discharge and 33 for the others.

The first two columns of ratios are again in general agreement with the phenomenon already established, and more especially when the breadths of the lines on the plate are taken into account. There is, in fact, no case of exception. But other important facts are brought out in this table. In the first place, the *stage* of energy transfer in this experiment is not quite the same as before, and it therefore depends on the circumstances of the experiment—perhaps on the pressure of gas and so on, and further work is required in order to test the possibility of transferring the energy further down the series. For one very interesting question which is raised is the possibility of transferring all the energy into the final members, so that the series would ultimately behave like a band so far as it is visible. But if this be possible,

the experimental conditions necessary to produce the effect cannot be as yet predicted.

HELIUM under Three Conditions.

λ.	h, (ord.).	h, (bulb).	$h_{\lambda}$ (bulb). $h_{\lambda}$ (cond.).		Photographic intensities.			Ratios of absolute central intensities.		
			K ·	Ord.	Bulb.	Cond.	Bulb/ord.	Cond./ord.	Cond./bulb.	
7065 6678 5876 5047 5015 4922 4713 4472 4388 4144 4121 4026	$ \begin{array}{c cccc}  & 7 \cdot 6 \\  & 14 \cdot 4 \\  & 16 \cdot 5 \\  & 2 \cdot 9 \\  & 11 \cdot 5 \\  & 7 \cdot 9 \\  & 10 \cdot 9 \\  & 14 \cdot 8 \\  & 5 \cdot 5 \\  & 1 \cdot 0 \\  & 3 \cdot 2 \\  & 5 \cdot 8 \\ \end{array} $	$ \begin{array}{c c}  & - & \\  & 10 \cdot 2 \\  & 14 \cdot 8 \\  & - & \\  & 7 \cdot 7 \\  & 9 \cdot 0 \\  & 9 \cdot 8 \\  & 16 \cdot 0 \\  & 7 \cdot 2 \\  & 2 \cdot 2 \\  & 3 \cdot 0 \\  & 6 \cdot 1 \end{array} $	$ \begin{array}{c}  - \\  10 \cdot 9 \\  16 \cdot 5 \\  \hline  8 \cdot 7 \\  7 \cdot 8 \\  9 \cdot 5 \\  15 \cdot 5 \\  7 \cdot 0 \\  1 \cdot 5 \\  4 \cdot 0 \\  6 \cdot 5 \end{array} $	$8 \cdot 13$ $61 \cdot 5$ $177 \cdot 8$ $2 \cdot 75$ $55 \cdot 2$ $17 \cdot 1$ $63 \cdot 1$ $442 \cdot 6$ $10 \cdot 5$ $1 \cdot 62$ $4 \cdot 72$ $20 \cdot 0$	$ \begin{array}{c}  - \\  18 \cdot 5 \\  104 \cdot 2 \\  - \\  14 \cdot 7 \\  25 \cdot 4 \\  41 \cdot 5 \\  726 \cdot 2 \\  21 \cdot 75 \\  2 \cdot 88 \\  4 \cdot 29 \\  23 \cdot 3 \end{array} $	20·6 152·8 ————————————————————————————————————	$\begin{array}{c c} - & - & \\ 0 \cdot 301 & \\ 0 \cdot 586 & \\ \hline - & \\ 0 \cdot 266 & \\ 1 \cdot 485 & \\ 0 \cdot 659 & \\ 1 \cdot 64 & \\ 2 \cdot 07 & \\ 1 \cdot 78 & \\ 0 \cdot 909 & \\ 1 \cdot 165 & \\ \end{array}$	$\begin{array}{c} -\\ 0 \cdot 335 \\ 0 \cdot 859 \\ -\\ 0 \cdot 346 \\ 0 \cdot 889 \\ 0 \cdot 528 \\ 1 \cdot 107 \\ 1 \cdot 74 \\ 1 \cdot 24 \\ 1 \cdot 39 \\ 1 \cdot 30 \\ \end{array}$	$ \begin{array}{c}                                     $	
3965 3888	$ \begin{array}{c} 2 \cdot 9 \\ 6 \cdot 6 \end{array} $	$3 \cdot 1$ $5 \cdot 2$	$3 \cdot 4$ $7 \cdot 4$	$\frac{4.75}{39.8}$	5·28 18·2	5·89 55·1	1·11 0·457	1·23 1·38	1·12 3·03	

Another interesting feature of this table is the evidence that the Principal series both of Helium ( $\lambda 3888$ ) and of Parhelium ( $\lambda \lambda 5015$  and 3965), are relatively enhanced with the condensed discharge as compared with the bulb.

## (VIII.) Transfer of Energy in the Hydrogen Spectrum.

The effects already described in connection with Helium are not peculiar to this gas. Experiments have been conducted in the same manner with Hydrogen, and with a mixture of Neon and Hydrogen. The results obtained from one of the typical experiments with this mixture may be given here, in so far as the Hydrogen spectrum is in question.

The lines  $H_a$ ,  $H_{\beta}$ ,  $H_{\gamma}$ ,  $H_{\delta}$ , are concerned, and the magnification of the wedge photographs is larger, being in this case such that the enlarged length of the wedge is 42 mm.

Hydrogen (with Neon).

λ.	D <sub>λ</sub> .	$h_{\lambda}$ (ord.).	$h_{\lambda}$ (bulb).	$D_{\lambda}h_{\lambda}/H$ (ord.).	$D_{\lambda}h_{\lambda}/H$ (bulb).	Photographic intensity (ord.).	Photographic intensity (bulb).	Central intensity ratio (bulb/ord.).
Η <sub>α</sub> Η <sub>β</sub> Η <sub>γ</sub> Η <sub>δ</sub>	$   \begin{array}{r}     4 \cdot 15 \\     5 \cdot 2 \\     6 \cdot 25 \\     7 \cdot 0   \end{array} $	15.6 13.8 11.5 5.3	$14 \cdot 7$ $14 \cdot 1$ $12 \cdot 6$ $6 \cdot 8$	1.541 $1.709$ $1.711$ $0.883$	1 · 453 1 · 746 1 · 875 1 · 133	$34 \cdot 8$ $51 \cdot 1$ $51 \cdot 4$ $7 \cdot 64$	28·4 55·7 75·0 13·6	0.816 1.090 1.459 1.780

Hydrogen evidently shows the effect in a more pronounced manner than Helium, in that the fourth line,  $H_{\delta}$ , shows it more than the third.

Our results are also in accordance with those of Sir J. J. Thomson\* who found that the intensity ratio  $\frac{H_{\beta}}{H_{\alpha}}$  was greater in the negative glow than in the positive column.

The enhancement of the later members of the Balmer series in the presence of Neon is in accordance with the observations of LIVEING and DEWAR† who found that it was possible to observe ultra-violet members of the series in a mixture of Neon and Helium containing Hydrogen, although these lines could not be found in vacuum tubes containing pure Hydrogen.

## (IX.) The Spectrum of Neon.

Except for certain series suggested by Rossi‡ involving only a few lines, the greater part of the Neon spectrum is of unknown structure, although some constant differences of frequency have been detected by Watson.§

One of the advantages of the mode of experiment described in this communication is that it may assist in elucidating the structure of very complicated spectra, and it may, in fact, be combined with investigations of the Zeeman effect, which has been used hitherto, as by Dufour in connection with the secondary spectrum of Hydrogen, in the detection of different classes of lines in such spectra. A preliminary examination of a portion of the Neon spectrum leads to some very interesting results which, however, at present cannot be brought within a general scheme of interpretation, owing to our lack of knowledge of series relations with which they are without doubt connected. The table contains a comparison of the spectra of Neon in the ordinary discharge and from the bulb, the gas containing a little Hydrogen. The enlarged length of the wedge was 42 mm. Only the stronger lines in the red and yellow have been subjected to examination, and if series exist in the spectrum, their leading members in the red and yellow should decrease considerably in intensity in the bulb, but on the whole, less considerably towards the yellow—provided that Neon behaves like Hydrogen and Helium.

There is a preponderance of small ratios in the case of the very strong lines, and the larger ratios are in general for the smaller wave-lengths, while the two smallest wave-lengths examined show enhancement, which is not found elsewhere in the list. These facts give some support to the view that a complicated system of series may be present. If, on the other hand, the spectrum is more in the nature of a band, as in

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' vol. 58, p. 244, 1895.

<sup>† &#</sup>x27;Roy. Soc. Proc.,' vol. 67, p. 467, 1900.

t 'Phil. Mag.,' XXVI., p. 981, 1913.

<sup>§ &#</sup>x27;Astrophys. Journ.,' XXXIII., p. 399, 1911.

<sup>|| &#</sup>x27;Ann. de Chim. et Phys.' (8) 9, p. 361, 1906.

NEON.

λ.	$h_{\lambda}$ (ord.).	$h_{\lambda}$ (bulb).	Photographic intensity (ord.).	Photographic intensity (bulb).	Ratio (bulb/ord.).	Tabular intensit (WATSON and BALY).
7032.6	6.7	$4 \cdot 2$	4 · 35	$2 \cdot 51$	0.578	3, —
6929 · 8	$9\cdot 2$	5.8	$7 \cdot 52$	$\frac{5}{3} \cdot \frac{5}{57}$	0.474	6. —
$6717 \cdot 2$	$17 \cdot \overline{6}$	$12 \cdot 2$	47.4	14.5	0.306	6, <del>-</del> 7, 1
6678.5	20.5	$12 \cdot \overline{5}$	$100 \cdot 3$	16.6	0.166	9, —
$6599 \cdot 2$	17.6	13.5	$52 \cdot 2$	20.8	0.398	9, 4
$6533 \cdot 1$	15.0	11.2	31.6	$12 \cdot 9$	0.417	6, 4
$6506 \cdot 7$	$27 \cdot 3$	17.0	$537 \cdot 0$	50.1	0.093	9, 6
$6402 \cdot 4$	$27 \cdot 3$	17.9	$537 \cdot 0$	$61 \cdot 7$	0.115	10, 10
6383 · 1	19.4	15.0	$87 \cdot 1$	31.6	0.363	9, 8
$6334 \cdot 6$	20.6	$16 \cdot 7$	$114 \cdot 9$	46.8	0.407	9, —
$6305 \cdot 0$	15.0	$12 \cdot 1$	31.6	$16 \cdot 2$	0.513	6, 8
$6266 \cdot 7$	20.0	14.4	111.5	$29 \cdot 8$	0.267	6, 10
$6217 \cdot 4$	13.8	10.6	2 <b>5</b> · 9	$12 \cdot 2$	0.470	6, 8
$6163 \cdot 7$	15.5	11.0	38.6	13.4	0.346	6, 10
$6143 \cdot 3$	21.6	19.0	162.6	88.1	0.542	7, 10
$6096 \cdot 4$	19.4	15.7	96.8	40.5	. 0.418	6, 10
$6074 \cdot 5$	16.0	14.8	$47 \cdot 4$	35.5	0.749	6, 10
$6030 \cdot 2$	11.0	9.0	$14 \cdot 2$	8.77	0.618	5, 10
$5975 \cdot *$	9.5	9.0	$9 \cdot 89$	8.77	0.887	5, 7
5945.0	16.3	13.7	51.0	$27 \cdot 2$	0.534	6, 10
5902.6	8.0	5.7	$7 \cdot 04$	$4 \cdot 02$	0.571	5, 4
5882.0	13.7	10.8	$28 \cdot 3$	13.9	0.493	5, 8
$5852 \cdot 6$	$24 \cdot 5$	16.0	421.7	51.8	0.123	10, 20
5820.3	5.8	6.0	4.18	4.40	1.050	5, 4
5764.5	8.0	10.0	$7 \cdot 19$	11.78	1.638	7, 8

<sup>\*</sup> A doublet,  $\lambda\lambda5974.8$  and 5975.8.

the corresponding region of the secondary spectrum of Hydrogen, the table contains the necessary information as to the variations of energy in the individual lines of such spectra. It is in any case noteworthy that the relative behaviour of the lines is very varied—and not comparatively uniform, as a mere visual inspection might suggest.

## (X.) Photographic Intensities in the Carbon Arc.

An inspection of Plate 1A, which contains a wedge-photograph of the Carbon arc, indicates the irregular behaviour of the photographic plate through the visible region. We have calculated already the absolute relative intensities in the Carbon arc when corrected for the dispersion adopted. Below are given the measurements and subsequent determination of the photographic intensities in the arc, as registered on a plate which contains the ordinary Helium spectrum examined in an individual case, through the wedge. On the arc is also superposed the ordinary Helium spectrum without the wedge, in order to identify positions of given wave-lengths, and to facilitate the measurements of the heights to which the arc photograph extends at

the various wave-lengths characteristic of Helium. The total length of the wedge on the magnified photograph is 32 mm., and the values of  $D_{\lambda}$ , the density of the wedge, are obtained from the previous graph already described.

CARBON	Arc,	H =	32	mm.
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λ.	$h_{_{\lambda}}.$	D <sub>λ</sub> .	$\mathrm{D}_{\lambda}h_{\lambda}/\mathrm{H}.$	Photographic intensity.	Ratios to value for 3888.	Absolute intensity ratio from previous table.
7065	17 · 3	3.95	2.135	136.6	13.7	28 · 98
6678	$23 \cdot 8$	4 · 1	3.049	1120	112.0	28.00
5876	21.8	4.5	3.066	1163	116.3	16.10
5047	$16 \cdot 7$	5.0	$2 \cdot 603$	401	40.1	7.04
5015	$17 \cdot 0$	5.0	$2 \cdot 656$	453	45.3	$6 \cdot 92$
4929	18.5	5.15	$2 \cdot 977$	949	94.9	6.08
4714	$19 \cdot 2$	5 · 45	$3 \cdot 270$	1863	186.3	4 · 475
4472	$16 \cdot 2$	5.9	2.987	970	97.0	$3 \cdot 02$
4438	$16 \cdot 0$	6.0	3.000	1000	100.0	$2 \cdot 73$
4388	$14\cdot 4$	6.13	2.758	573	57.3	2.56
4143	10.1	6.9	2.178	150.6	15.06	$1 \cdot 73$
4121	$9 \cdot 9$	$6 \cdot 95$	2.026	106.3	10.63	1.61
4026	$7\cdot 4$	$7 \cdot 4$	1.711	51.4	5.14	1.31
3965	$5 \cdot 7$	$7 \cdot 7$	$1 \cdot 372$	$23 \cdot 54$	$2 \cdot 35$	1.17
3888	4.0	8.0	1.000	10.00	1.00	1.00

It is evident from the last two columns that the photographic effect is a very complicated function of wave-length, and that the present method of using the same plate for the standard spectrum and that to be measured is the only one which can give quantitative values for intensity, with a real physical significance.

Measurements of the ordinary spectrum of Helium on an adjacent portion of the same plate give the results shown in the next table.

Helium (Ordinary Discharge), H = 32 mm.

- λ.	$h_{\lambda}$ .	$h_{\lambda} \mathrm{D}_{\lambda} / \mathrm{H}.$	Photographic intensity.	λ.	$h_{\lambda}$ .	$h_{\lambda} \mathrm{D}_{\lambda} / \mathrm{H}$ .	Photographic intensity.
7065 6678 5876 5044 5015 4932 4714	4·5 11·8 14·4 2·9 10·3 8·3 10·5	0.555 $1.512$ $2.025$ $0.453$ $1.609$ $1.336$ $1.788$	$3 \cdot 594$ $32 \cdot 5$ $105 \cdot 9$ $2 \cdot 839$ $40 \cdot 7$ $21 \cdot 7$ $61 \cdot 4$	4472 4388 4121 4026 3965 3888	13·8 5·5 3·0 5·4 3·0 8·0	$ \begin{array}{c} 2 \cdot 544 \\ 1 \cdot 054 \\ 0 \cdot 651 \\ 1 \cdot 249 \\ 0 \cdot 719 \\ 2 \cdot 00 \end{array} $	$350 \cdot 2$ $11 \cdot 3$ $4 \cdot 48$ $17 \cdot 7$ $5 \cdot 23$ $100$

The lines  $\lambda\lambda 4438$ , 4143 are omitted, for they were too weak to admit of accurate measurement.

These tables contain all the necessary data for the calculations of the relative central maxima of intensity of the Helium lines, according to the formula,

(photo. intensity of line) (absolute intensity of arc)/(photo. intensity of arc),

to which they are proportional. This calculation is exhibited in the next table, and it is convenient to take some definite line as the standard. For this purpose  $\lambda 3888$  has been selected. The table contains the real intensity maxima of all the important lines relatively to that of  $\lambda 3888$ , measured on an absolute scale, and produced by the ordinary discharge.

(XI.) Relative Intensities of Helium Lines on an Absolute Scale.\*

Ordinary Discharge.

λ.	Photographic intensity of line $(\alpha)$ .	Photographic intensity of arc $(\beta)$ .	Absolute intensity of arc $(\gamma)$ .	Absolute intensity of helium $(\alpha \gamma/\beta)$ .	Tabular intensity (RUNGE and PASCHEN).
7065	$3 \cdot 594$	13.7	28.98	$7 \cdot 61$	5
6678	$32 \cdot 5$	112.0	28.00	$8 \cdot 12$	6
5876	105.9	116.3	16:10	$14 \cdot 7$	10
5048	2.839	40.1	$7 \cdot 04$	0.498	2
5015	$40 \cdot 7$	45.3	$6 \cdot 92$	$6 \cdot 22$	6
4922	$21 \cdot 7$	94.9	6.08	$1 \cdot 39$	4
4714	61.4	186 · 3	$4 \cdot 475$	$1 \cdot 47$	3
4472	$350 \cdot 2$	97.0	$3 \cdot 02$	10.90	6
4388	11.3	57 · 3	$2 \cdot 56$	0.505	3
4121	4 · 48	10.63	1.61	0.678	3
4026	17.7	5.14	$1 \cdot 31$	4.51	5
3965	$5 \cdot 23$	$2 \cdot 35$	$1 \cdot 17$	$2 \cdot 60$	4
3888	100.0	1.00	1.10	100.0	10

The most remarkable feature of the table is the strength of  $\lambda 3888$ , the first visible member of the Principal series of Helium, which is much stronger than any of the lines of the two Subordinate series. Moreover, of the Parhelium lines,  $\lambda\lambda 6678$ , 4922, 4388, (Diffuse),  $\lambda 5048$  (Sharp) and  $\lambda\lambda 5015$ , 3965 (Principal), the Sharp line is very weak, and the third member of the Principal series is stronger than that of the Diffuse—the first member of the Principal series is in the infra-red. It is evident, therefore, that under ordinary conditions, the two Principal series of Helium actually deserve their title. This extension to Helium of a result with which spectroscopists are familiar in some

<sup>\*</sup> In a previous section we have given a table of the photographic intensities. We have done so, at the risk perhaps of some repetition, because we believe that the values given for photographic intensities are worthy of some confidence, and in the event of more accurate data being at some future time available for the temperature of the carbon arc, the accuracy of our "absolute intensities" can at once be correspondingly enhanced by a simple recalculation.

other elements is of importance in that it suggests that, under ordinary conditions, the Principal series of an element always contains the most important part of the radiation. This point has hitherto been obscured on account of the vagaries of the photographic plate and of the eye. It is interesting to compare the absolute intensities of members of any one series. For example, in the Diffuse series of Parhelium,  $\lambda\lambda6678$ , 4922, 4388, the intensities are 8.12, 1.39, 0.505, or roughly in the ratio 16:6:1, which fall much more rapidly than the usual tabular intensities.

In the Diffuse series of Helium,  $\lambda\lambda 5876$ , 4472, 4026, the ratios are approximately 3.3, 2.4, 1, and in the Sharp series  $\lambda\lambda 7065$ , 4714, 4121, they are 11.2, 2.2, 1, so that the Diffuse series of Helium falls off less rapidly than the others.

The discussion given already of the phenomenon of transfer of energy down the spectrum towards the violet is perhaps sufficiently complete. It is, however, interesting to append a table of the relative absolute intensities of the Helium lines, under various conditions, with that of  $\lambda 3888$  taken arbitrarily as 100. The results are deduced at once by a combination of the last table with those in previous sections, where the relative phenomena exhibited by the *same* line were examined. The following are the final results of the calculation:—

APSOLUTE	Intensities	of Helium	Lines
- A BSOLUTE	THEERSTHES	or renum	LITTLES.

λ.	Intensity (ordinary discharge).	Intensity (bulb).	Intensity (condensed discharge).
7065	7.61	1.03	very small
6678	$8 \cdot 12$	$2 \cdot 20$	3.30
5876	$14 \cdot 7$	9.58	14.7
5044	0.498	very small	very small
5015	$6 \cdot 22$	ĭ·84	3.71
4922	1 · 39	$1\cdot 25$	1.88
4714	1 · 47	0.606	1.76
4472	10.90	$36 \cdot 2$	10.90
4388	0.505	0.737	1.42
4121	0.678	0.618	$1 \cdot 356$
4026	$4 \cdot 51$	11.73	4.51
3965	2.60	$2 \cdot 60$	3.18
3888	100.0	$23 \cdot 2$	72.9

The extraordinary enhancement of  $\lambda 4472$  in the bulb, and to a smaller extent, of  $\lambda 4026$ , is shown in a striking way in this table, together with the weakening of  $\lambda 5876$ . For other points of interest, it is perhaps sufficient to refer back to the discussion of energy-transfer already given, but this table also indicates that the transfer takes place to a great extent also at the expense of the Principal series.

It is perhaps unnecessary to give the detailed working out of corresponding

problems in connection with the Balmer series, and only the final results are therefore exhibited. They are as follows, in the case of the ordinary discharge:—

ngmage.	O 7.	T .	. ,
Hydrogen,	Ordin	arv D	ischarge.
ALL I DIO GIANO	O I CILL	.ccz y .zc	ibolitary or

λ.	Photographic intensity.	Photographic intensity of are.	Absolute intensity of arc.	Absolute intensity of hydrogen lines.
$egin{array}{c} H_{lpha} \ H_{eta} \ H_{\gamma} \ H_{\delta} \end{array}$	$22 \cdot 08$ $25 \cdot 06$ $17 \cdot 18$ $2 \cdot 34$	$141 \cdot 7$ $131 \cdot 8$ $54 \cdot 25$ $8 \cdot 00$	26.51 $5.68$ $2.39$ $1.55$	$4 \cdot 13$ $1 \cdot 08$ $0 \cdot 757$ $0 \cdot 453$

The fall of absolute intensity down the series proceeds fairly regularly. The measurements of the photographs of the Hydrogen spectrum taken in the presence of Neon give an estimate of the extent to which a large admixture of Neon affects the intensities of the lines. The particulars are contained in the following table:—

#### Hydrogen mixed with Neon.

λ.	Intensity in hydrogen (ordinary discharge).	Intensity in hydrogen and neon (ordinary discharge).	Intensity in hydrogen and neon (bulb).
$H_a$ $H_{\beta}$ $H_{\gamma}$ $H_{\delta}$	4·13 1·08 0·767 0·453	$6 \cdot 51$ $2 \cdot 20$ $2 \cdot 26$ $1 \cdot 48$	5·31 2·40 3·30 2·63

The enhancement of the later members of the series by Neon is very extraordinary, and is even more striking in the bulb than in the capillary.

#### (XII.) The Nature of the Balmer Series.

The investigation of the effect of Neon on the Hydrogen lines when produced in its presence, for which some quantitative data are given in the last section, cannot be interpreted in a satisfactory manner without a precise knowledge of the nature of the Balmer series. For in the case of Helium, the series arrangement into Principal and Subordinate series is known precisely, and considerable differences have been found in the behaviour of the three types; more especially the Principal series behaves in a quite different manner from the other two. Until the type to which the Balmer series belongs is known, moreover, no discussion of the relative behaviour of

Hydrogen and Helium under similar conditions is possible. We are thus led directly to a problem which has many other important implications, some of which are stated below.

In the earlier paper\* we suggested that the neutral-tinted wedge, as an accessory to the spectroscope, virtually increased the resolving power, and that in combination with the interferometer it should be able to solve problems which are beyond the power of pure spectroscopic analysis in its ordinary forms. Some experiments have been performed in connection with what is perhaps the most urgent of these problems at the present time—the elucidation of the nature of the Balmer series of Hydrogen. It has been generally accepted for some time that the series is one of doublets—we are not, at the present juncture, considering some very recent theoretical work by Sommerfeld—but the exact nature of the series has always been an open question. For if it corresponds to a subordinate series (Diffuse or Sharp) in other elements, the separations in wave-number of the two components should be identical along the series. If, on the other hand, it corresponds to a Principal series, the separations should decrease rapidly towards the violet, after a manner which can be calculated from the separation in H<sub>a</sub>, the first member of the series. There is at present no precise knowledge of the nature of these separations. Michelson† found  $H_a$  to be a doublet of separation 0.14, the intensities of the components being in the ratio 10:7, and the stronger one being on the red side. On the other hand, in  $H_{\beta}$  he found a separation only half as great, and the lines were so broad that no great degree of accuracy could be attached to this value. Others who have investigated the separation of H<sub>a</sub> have obtained very discordant values. Thus Houstount gives 0.065, Fabry and Buisson 0.132, and Paschen and Back 0.20, so that there is no certain knowledge even as regards the separation of H<sub>a</sub>. Fabry and Buisson have also stated that  $H_{\beta}$  is double, with a separation in accordance with the theoretical value. statement is somewhat vague, especially as no numerical estimate was given, and the theoretical separation depends very much on the view we take as to the character of the series. For example, with Michelson's value for  $H_a$ ,  $\delta\lambda = 0.14$ , the separation in  $H_{\beta}$  as a Diffuse or Sharp member would be

$$\delta \lambda' = 0.14 (4861)^2 / (6563)^2 = 0.075 \text{ Å.U.},$$

but as a member of a Principal series would only be

$$\delta \lambda'' = 3^3 \delta \lambda' / 4^3 = 0.031 \text{ Å.U.}$$

An experimental arrangement, therefore, of more sensitiveness than any used

<sup>\*</sup> Loc. cit.

<sup>† &#</sup>x27;Phil. Mag.,' (5), vol. 34, p. 282, 1892.

<sup>‡ &#</sup>x27;Phil. Mag.,' (6), vol. 7, p. 456, 1904.

<sup>§ &#</sup>x27;Journ. de Phys.,' June, 1912.

<sup>|| &#</sup>x27;Ann. der Phys.,' 39, p. 897, 1912.

hitherto, which could determine precisely an upper limit sufficiently low for the possible separation of  $H_{\beta}$ , would be decisive between these two alternatives, if the Michelson value were correct for  $H_{\alpha}$ , but if Houstoun's value were correct, such an experiment for  $H_{\beta}$  would be much more difficult to perform. It is necessary, therefore, as an essential preliminary to an attack on this problem, to repeat the measurement of the separation in  $H_{\alpha}$  in order to determine the possible magnitudes in the case of  $H_{\beta}$ .

Other possible interpretations of the Balmer series have been proposed, and these consist mainly in regarding it as a set of two or more practically coincident series. This has been suggested, for example, by Fowler,\* but it appears to involve a more complicated structure than doublets for the individual lines of the series. At the same time, it does not at present violate any definite experimental knowledge. Exact superposition of series cannot, however, be expected even in the case of Hydrogen. Hypotheses of this type are virtually a combination of the two alternatives already suggested, and an experiment which could decide between these two alternatives could, of necessity, also give a verdict for or against the present one. For it would apparently be necessary in this case that  $H_a$  should be a triplet.

From the point of view of series relations, another alternative, which has apparently not been noticed hitherto, may be put forward at this juncture. The Balmer series may primarily be a series of single lines, and the other components may be combination lines nearly coincident with these. If the normal series is given by Curtis's formula

$$n = N \left\{ \frac{1}{(2+p)^2} - \frac{1}{(m+\mu)^2} \right\}$$

where N = 109679.2, p is negligible, and  $\mu = 0.000007$ , then the Principal series may be that of Lyman in the Schumann region, following the law

$$n = N \left\{ \frac{1}{(1+p)^2} - \frac{1}{(m+\mu)^2} \right\}.$$

Combinations of an Arc series with itself are now well established if it is a Principal series, and on the present view we should expect a combination series of the form

$$n = N \left\{ \frac{1}{(2+\mu)^2} - \frac{1}{(m+\mu)^2} \right\}$$

with a constant difference of wave number from that of Curtis, of amount  $N(2+p)^{-2}-N(2+\mu)^{-2}=0.192$  on calculation. The corresponding separations of  $H_a$  and  $H_{\beta}$  then become 0.081, 0.048 Å.U. respectively, the first being nearer to Houstoun's estimate. There should also be a series

$$n = N \left\{ \frac{1}{(2+\mu)^2} - \frac{1}{(m+\mu)^2} \right\}$$

\* 'Bakerian Lecture,' 1914.

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very nearly coincident with the Balmer series, and this leads to separations in wave number which are not constant. The values for  $H_{\alpha}$  and  $H_{\beta}$  are respectively  $\delta n_1 = 0.248$ ,  $\delta n_2 = 0.218$ , and the corresponding separations in wave-length become

$$\delta \lambda_1 = 0.105, \quad \delta \lambda_2 = 0.054 \text{ A.U.}$$

These are nearer to Michelson's estimate. It is just possible, therefore, that the presence of these two series with different intensities under different conditions may be the cause of the discrepancies which have been found in the separation of H<sub>a</sub>. We do not at present pursue the subject beyond this conclusion, but it may be stated that such a view could give an account of the spectrum of Hydrogen, as at present known, which is in accord with the series relations known among other elements. The possibility of this new interpretation, in addition to such interpretations as that given by Fowler, only serves to emphasise the need for an examination of the structure of the Balmer lines, which alone can be decisive. Another fundamental question with an intimate relation to the preceding remarks is the value of the Rydberg constant N for Hydrogen. The careful reduction of this value by Curtis\* depends ultimately on an accurate determination of the optical "centre of gravity" of the leading Balmer lines, and his formula is not applicable to the individual components. If the separations of  $H_{\alpha}$  and  $H_{\beta}$  were very different, this formula and its contained value of N would cease to represent the series for any individual components, or even to give a series lying uniformly between two component series, and the value of N would need revision. In view of the theoretical importance which the exact value of N for Hydrogen and for Helium has recently assumed, it is necessary that the true value should not remain a matter of doubt, and only a precise determination of the separations can decide the question. If for example, the separation in  $H_{\beta}$  were found to be of the same order as that of a Principal series, a very important correction would be necessary in the observed wave-length of the optical centre of  $H_{\beta}$  which might change N very appreciably. This, in fact, as is shown by the experiments to be described later, actually occurs.

# (XIII.) Theoretical Considerations on the Basis of the Quantum Theory.

Sommerfeld\* has recently published a remarkable investigation on the fine structure of the lines of the Balmer series. This is based on Bohr's theory of the origin of this series, and it represents the only manner in which this theory at present can be applied in order to account for the existence of structure. On the view that the Hydrogen atom consists of one electron in orbital motion—its path being circular or elliptical—about a positively charged nucleus, with steady states characterised by discrete values of the angular momentum, the quantum theory requires the emission

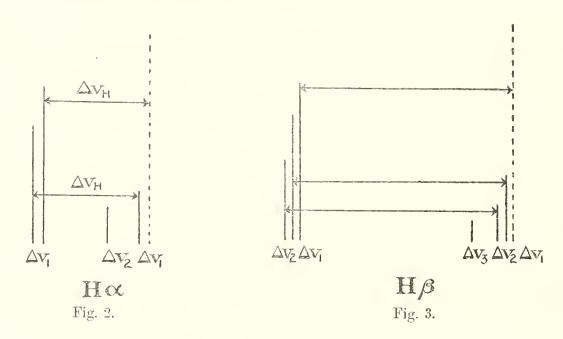
<sup>\*</sup> Loc. cit.

<sup>† &#</sup>x27;Sitz. der K. Bayr. Akad., München,' Jahrgang, 1916.

of a frequency  $\nu$  where, if h is Planck's constant,  $h\nu$  is the difference of energy between two states—when the electron passes from one state to the other. In the case of elliptic motion, Sommerfeld finds it necessary for certain purposes to confine the eccentricities of the possible ellipses to definite discrete values, and thus obtains spectral lines which are not single, as in Bohr's theory in its ordinary form, but which have a definite structure. In fact, his theory involves the supposition that the Balmer series is effectively a supposition of Diffuse, Sharp and Principal series, as in some of the suggestions mentioned in the last section. These series are superposed in the case of Hydrogen, on account of the simplicity of the atom, and general considerations indicate—though not with great precision—that they would be widely separated in the case of other elements. This is not the appropriate place for any discussion or exposition of the theory, for we are concerned solely with the actual structure to which it leads.

The most important result is that the separation in  $H_{\beta}$  is of the order suitable for a Diffuse or Sharp series, in comparison with that of  $H_{\alpha}$ . The latter is used—Buisson and Fabry's value  $\delta\nu_{\rm H}=0.307$ , corresponding to  $\delta\lambda=0.132$  Å.U.—to determine a constant of the investigation, and the other separations are deduced in terms of this value. The results are as follows:—

In  $H_a$  the complete structure is that shown in fig. 2, where the separations are



shown on a wave-number scale. The "main" separation is called  $\delta \nu_{\rm H}$ , and the "satellite" separations are  $\delta \nu_{\rm I}$ ,  $\delta \nu_{\rm 2}$ , where

$$\delta \nu_1 = \frac{8}{81} \delta \nu_{\rm H}, \qquad \delta \nu_2 = \frac{8}{27} \delta \nu_{\rm H} = 3 \delta \nu_{\rm I}.$$

Since  $\delta v_{\rm H} = 0.307$ , we have

$$\delta \nu_1 = 0.030, \quad \delta \nu_2 = 0.090,$$

and the corresponding wave-length differences are

$$\delta \lambda_1 = 0.013 \text{ Å.U.}, \qquad \delta \lambda_2 = 0.039 \text{ Å.U.}$$

The diffuse character of the components of  $H_a$  would render it practically impossible to detect so small a quantity as  $\delta\lambda_1$  by any method, and since  $\delta\lambda_2$  gives a weak component falling inside the main components, which themselves nearly overlap, the satellite corresponding to  $\delta\lambda_2$  could not be expected either.

The structure for  $H_{\beta}$  is shown in fig. 3, and is more complex. The values of the separations indicated in the figure are :—

$$\delta\nu_1 = \frac{1}{48} \delta\nu_H, \qquad \delta\nu_2 = \frac{1}{24} \delta\nu_H, \qquad \delta\nu_3 = \frac{1}{8} \delta\nu_H,$$

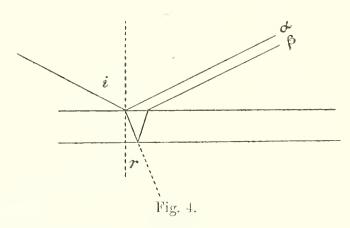
and all the satellites are even more difficult to detect than those of  $H_{\alpha}$ .

The most fundamental test of the theory, however, in a preliminary form, is to decide whether the main separation is again  $\delta \nu_{\rm H}$ . If it is smaller and of the magnitude required in a Principal series, the theory would apparently not hold. We confine ourselves for the present to a presentation of the results, and further discussion follows after the description and measurements of the plates.

The main theoretical features of this somewhat complex problem are now defined, and we may proceed to the experimental method. This consists merely in the use of a Lummer Gehrcke plate in addition to the former apparatus, the interference fringes being brought to a focus on the slit through the neutral wedge. The final pattern which is photographed—again with the use of the process screen—for any line such as  $H\alpha$  consists of a set of fringes of the various orders. These consist of similar curves, with a general parabolic appearance, and approximately equidistant. From the shape of the contour of any one of these curves, we can deduce mathematically its analysis into components, from which by knowledge also of the density of the wedge the separations and relative intensities on an absolute scale of the components in the original light can be found,

The ordinary theory of the action of a Lummer Gehrcke plate on monochromatic light is, of course, familiar, but in its extension to a problem of this nature it becomes somewhat cumbrous. We have found it possible, however, to devise a more simple treatment of the theory of the plate which can be applied not only to the present case but apparently to all practical cases in which the use of the plate is necessary. We append, therefore, an account of this method, which is to some extent empirical, although it is not difficult to show that it is equally accurate. It is rendered the more necessary in that even the strict theory has apparently not been worked out completely for lines which are not monochromatic, but have a definite breadth as in the present experiments, where in fact the breadth is itself a matter of investigation.

The ordinary theory of the Lummer Gehrcke plate is, as stated above, well known so far as monochromatic radiation is concerned. If light falls on the plate, as in the figure (fig. 4), and if  $\alpha$  and  $\beta$  are the rays respectively reflected once, and refracted twice and reflected once, their path difference is  $D = 2 \mu d \cos r$  where  $\mu$  is the index of the plate for the particular wave-length, r is the angle of refraction, and d is the thickness of the plate. When the complete system of multiple reflections is considered,



and the interfering rays are focussed on a screen S, the intensity corresponding to the angle of refraction r is

$$\frac{4a^2\tau \sin^2(\pi D/\lambda)}{(1-\tau)^2 + 4\tau \sin^2(\pi D/\lambda)}$$

where  $\lambda$  is the wave-length,  $a^2$  is the intensity of the incident light, and  $\tau$  is the square of the internal reflection coefficient of amplitude, such that, for light polarized parallel to the plane of incidence, by Fresnel's formula

$$\tau = \tan^2(\iota - r)/\tan^2(\iota + r),$$

but for light polarized perpendicular to this plane,

$$\tau = \sin^2(\iota - r)/\sin^2(\iota + r).$$

Maxima occur on the screen when  $D = \frac{1}{2} n\lambda$  if n is an odd integer, and minima when n is even.

As regards the nature of these maxima and minima, a full discussion may be found, for example, in Gehreke's treatise.\* It is not difficult to show that in order to obtain very sharp maxima nearly grazing incidence must be employed, so that  $\tau$  is nearly unity, and this is adopted in the present experiments.

When we pass from this ordinary theory to the problem now in hand, difficulties begin to appear. In the first place,  $D = 2\mu d \cos r$  is not actually a constant, although it may be nearly so for several successive maxima if the order is high. The successive separations of the maxima are therefore not identical, and there is also a variation in their intensities. This effect could be calculated, but owing to the

<sup>\* &#</sup>x27;Anwendung der Interferenzen,' Braunschweig, 1916.

difficulty of securing uniform illumination, such a calculation would be of no value. If measurements of the pattern to a high order of accuracy are required, it must in the first place be made "normal" in a manner subsequently explained. The variation in distance apart of the maxima is, in fact, in the present experiments, very small, as will appear from the measurements, and a high degree of accuracy could have been obtained by neglecting it.

The most important linear magnitude in the pattern, when it is obtained for two spectrum lines close together, whose separation is to be deduced, is, of course, the difference of wave-length corresponding to the distance between successive orders. Variations in D can be allowed for by making the pattern normal, and we may treat D as constant in the present theoretical investigation. Its value is

$$D = 2\mu d \cos r$$
,

or, for grazing incidence, for which  $\sin r = 1/\mu$ ,

D = 
$$2\mu d \cos \sin^{-1} \left(\frac{1}{\mu}\right) = 2d \left(\mu^2 - 1\right)^{1/2}$$
.

Between successive maxima,  $\pi D/\lambda$  increases by  $\pi$ , and, therefore, if  $\lambda' - \lambda$  is the wavelength separation corresponding to the distance between these maxima on the photograph,

$$\frac{\pi D}{\lambda} - \frac{\pi D}{\lambda'} = \pi$$
, or  $\lambda' - \lambda = \lambda \lambda' / D$ .

To a first approximation,  $\lambda' - \lambda = \lambda^2/D$ . We may denote this quantity by  $\epsilon$ , and

$$\epsilon = \lambda^2/2d(\mu^2-1)^{1/2}.$$

The accurate value is  $\epsilon = \lambda^2/(D-\lambda)$ , but its use would never be required. For a given plate,  $\epsilon$  may be tabulated in a form suitable for interpolation. We have in this manner calibrated the plate used in these experiments. The plate was supplied by Messrs. Hilger, and its indices of refraction for the yellow sodium line and for the lines  $H_a$ ,  $H_\beta$ ,  $H_\gamma$  were known with great precision. With the old notation, C, D, F, G, for these lines, the values were:—

$$\mu_{\rm G} = 1.50746, \qquad \mu_{\rm D} = 1.50990, \qquad \mu_{\rm F} = 1.51560, \qquad \mu_{\rm G} = 1.52025,$$

and the thickness of the plate was d = 4.439 mm.

The corresponding calculated values of  $\epsilon$  are:—

$$\epsilon_{\rm C} = 0.43010, \qquad \epsilon_{\rm D} = 0.34615, \qquad \epsilon_{\rm F} = 0.23376, \qquad \epsilon_{\rm G} = 0.18533,$$

and they fit the interpolation formula

$$\epsilon_{\lambda} = 0.1853 + 0.8786 (\lambda - 4341) + 0.0001 (\lambda - 4341)^2$$

with great accuracy. By means of this formula, the plate can be calibrated for all wave-lengths, but for the present purpose, only the values  $\epsilon = 0.4301$ , 0.23376 for  $H_{\alpha}$  and  $H_{\beta}$  are required.

Since the lines have a definite width, the theory outlined above is not strictly applicable in its entirety, but if the resolving power of the instrument is great in comparison with the observed (apparent) widths of the lines, it is well known that the maximum for any one wave-length is not altered except in magnitude, and that the plate gives reproductions of the lines in the successive orders with only a change in intensity—which is uniform along the narrow line—of each of the infinite number of components into which it can be resolved theoretically. Without the use of the plate, the wedge photograph should be parabolic for each line in the ordinary discharge as proved in a former paper\*—according to the ordinary theory of broadening—and the combination of wedge and plate should, therefore, also give parabolic traces on the photograph under the condition that the lines are sufficiently narrow. This condition appears to be fulfilled in the case of the Hydrogen lines, and, in fact, it is proved later that the traces on the plate, when reduced to a normal pattern, are very accurately parabolic.

Reduction of the Fringes to a Normal Standard.—We have seen that in the case of a line broadened according to the probability law of intensity the fringes obtained from the wedge and plate should be a series of blackened patches with parabolic contours. Owing to the small variation of D, the path difference produced by two refractions in the plate, the parabolas are not uniform. They are not at equal intervals, and the distances between their axes must increase from the central member of the set of fringes. Their heights also vary continuously, and the appearance of the maximum heights of the individual fringes is as shown in the

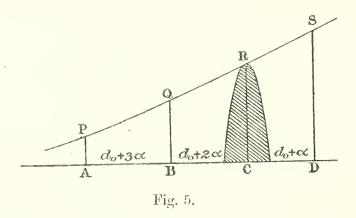


figure (fig. 5), where PA, QB, RC, SD, are four successive heights, and AB, BC, CD are in descending order of magnitude.

A theoretical consideration of the angle of refraction—nearly equal to  $\sin^{-1}\left(\frac{1}{\mu}\right)$ , corresponding to each fringe, shows that the distance, say AB, between the  $n^{\text{th}}$  and

n+1<sup>th</sup> fringe should be very accurately given by the formula  $\alpha+\beta n$  where  $\alpha$  and  $\beta$  are constant. In other words, these distances are in arithmetical progression. Measurement of the plates shows that this law is almost exactly fulfilled in our photographs, the term in  $n^2$ , which would follow, having so small a coefficient as to be negligible for fringes not too far from the central one—signifying, in practice, the first five or six. This inequality of dispersion of the plate could be corrected graphically, but a simple interpolation formula deduced as follows is more convenient, for it elucidates the principal effects in a clear manner.

Let  $d_0$  be the "normal" interval between two maxima, for a certain uniform dispersion, and  $d_0+\alpha_3$ ,  $d_0+2\alpha$ , ..., the intervals actually found. Thus  $d_0$  is the interval corresponding to the wave-length separation  $\epsilon$ . The intervals  $d_0+\alpha$ ,  $d_0+2\alpha$  are DC, CB, in the figure, and may be called p and q. Then

$$d_0 = 2p - q$$

gives the normal scale to which the fringe of axis RC is being reduced. The whole visible fringe for this axis is shaded in the figure.

The law of the intervals between the fringes can be expressed by the formula

$$z' = z \left( 1 + \frac{\alpha}{2d_0} \right) + \frac{\alpha z^2}{2d_0^2}$$

where a "normal" interval z reckoned from any specified starting point becomes z' on the photograph. Thus if  $z = d_0$ ,  $z' = d_0 + \alpha$ , and if  $z = 2d_0$ ,  $z' = (d_0 + \alpha) + (d_0 + 2\alpha)$ . A line of breadth x on the normal scale, on one side of the point  $d_0$ , becomes situated at the point  $d'_0 + x'$  on the photograph, where

$$d'_{0} + x' = (d_{0} + x) \left(1 + \frac{\alpha}{2d_{0}}\right) + \frac{\alpha}{2d_{0}^{-2}} (d_{0} + x)^{2},$$

and as  $d'_0 = d_0 + \alpha$ , we find

$$x' = x + \frac{3}{2} \frac{x\alpha}{\bar{d_0}} + \frac{x^2\alpha}{2\bar{d_0}^2}.$$

There is a difference between the right and left sides of the central line in the figure of the fringe. For on the left x' is positive, and on the right it is negative, while the last term in this formula is always positive. Thus the fringes are distorted—shortened on one side and expanded on the other. If x' is the breadth on the right, and x'' on the left, corresponding to a normal breadth x on either side

$$x' = x \left( 1 + \frac{3\alpha}{2d_0} \right) + \frac{\alpha x^2}{2d_0^2}, \qquad x'' = x \left( 1 + \frac{3\alpha}{2d_0} \right) - \frac{\alpha x^2}{2d_0^2},$$

whence

$$x' + x'' = 2x \left(1 + \frac{3\alpha}{2d_0}\right),$$

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where  $d_0 = 2p - q$ , and the normal breadth  $d_0 = 2p - q$ , and the normal breadth  $d_0 = 2p - q$ , and the normal interval  $d_0 = 2p - q$ , and the normal breadth of the distorted parabolic fringe is the true normal breadth. In other words, if p and q are the observed intervals on the right and left of any fringe, the normal interval corresponding to  $\epsilon$  has a length  $d_0 + \frac{3\alpha}{2}$ , where  $d_0 = 2p - q$ ,  $\alpha = q - p$ , and the central fringe is on the right. This length becomes  $\frac{1}{2}(p+q)$ , or the mean of the observed intervals. On this scale the apparent breadth of a distorted fringe is the true breadth of the undistorted one, if it is symmetrical about the central line when undistorted.

In this normal system, the apparent breadth on the right, of a real breadth x, is

$$x' = x - \frac{\alpha x^2}{2d_0^2}$$

to a sufficient order, and on the left,

$$x'' = x + \frac{\alpha x^2}{2d_0^2}.$$

Conversely, the real breadths on this normal scale corresponding to observed breadths x' and x'' are

$$x = x' + \frac{\alpha x'^2}{2d_0^2}, \qquad x = x'' - \frac{\alpha x''^2}{2d_0^2}$$

when insignificant terms are neglected. These results enable us in the next section to isolate the individual components of a broadened line, and to obtain their separation.

The second manner in which the fringes are not normal is in regard to their heights. This effect has a much smaller influence on the contours of the individual fringes, although it appears as a striking phenomenon in itself on the photographs. A theoretical investigation, which need not be reproduced here, indicates that the summits of the maxima—P, Q, R, S, in the preceding figure—should lie almost exactly on a parabola when the light falls on the plate at nearly grazing incidence. This parabolic locus of the summits is indicated on the photographs, but in actual fact the parabola is very nearly a straight line. Indeed, a straight line can be passed with some precision through any three consecutive summits, and it has been found sufficient, for the degree of accuracy we desired to obtain, to consider only three summits, so that the straight line locus can be used. For any given fringe, say CR in the figure, the "normal" heights of points on the right must be slightly smaller than the observed values, and those of points on the left must be slightly larger.

If axes are taken at C, the axis of y being along CR, and of x along CD towards the right, and if the equation to the "normal" parabola is

$$-kx^2 = y - h, \qquad h = CR,$$

then the equation to the parabola distorted by this effect should be

$$-kx^{2} = y - h - \frac{h' - h}{d_{0}}x, \qquad h' = DS,$$

for the height increases from the normal value at a rate  $(h'-h)/d_0$  very closely for a unit increase in x, when x is positive. It decreases at the same rate when x is negative, or to the left, so that both sides of the distorted curve are included. As stated above, the correction is, in fact, not very important in the subsequent calculations, its inclusion affecting only the third significant figure in the final separation of the components deduced in the case of  $H_{\alpha}$ . In a calculation of separation, or distance between the axes of two overlapping parabolas, the effect along x is naturally the more significant.

# (XV.) The Law of Intensity Distribution in a Line Excited by the Ordinary Discharge.

No direct proof of the validity of the usual law obtained for the intensity distribution around the maximum in a line broadened by the ordinary discharge—the law of probability  $I = I_0 \exp(-k^2\lambda^2)$ —has been given hitherto, although the work of Lord Rayleigh\* and Schönrock has placed it on a secure theoretical basis, subject to certain well understood limitations in the conditions of excitement. It forms the basis of the calculations of atomic weights and emission temperatures of sources, made from the results of such experiments as those of Buisson and Fabry†, and on this ground it is desirable that it should be confirmed experimentally in at least one definite case, for it is not possible to foretell readily whether the theoretical conditions are satisfied in any practical case. Moreover, we showed in the previous paper that it breaks down completely in the condensed discharge, and that all the components into which the line is then split by the electrical resolution which takes place under these circumstances follow the exponential law  $I = I_0 \exp(-k\lambda)$ . From the present photographs, it is possible to give a direct proof of the applicability of the theory to the ordinary discharge in Hydrogen. For all that is necessary is to show that the individual contours of the components making up, say  $H_a$ , are strictly parabolic.

Inspection of the photographs indicates that both  $H_a$  and  $H_\beta$  are double, and that each component is represented by a contour which appears very definitely parabolic—with, of course, the slight distortions dealt with in the preceding section. The parabolas overlap and represent lines of different intensities. We have not attempted to measure these intensities in the present experiments, but, as judged from the heights of the parabolas—one of these is calculated from the visible part of the contour—they are in at least rough accordance with Michelson's† estimate of 10 to 7. The

<sup>\* &#</sup>x27;Phil. Mag.,' XXIX., p. 274, 1915.

<sup>†</sup> Loc. cit.

contours intersect in a definite kink on one side of the main contour, and sufficiently above this kink the contour entirely represents the stronger component only and its exact form can be found. There is no evidence of any third component. Measurements have shown that the parabolic form is very exact for this stronger component, and as an illustration of the degree of exactness obtained, we append one calculation made from a single plate—which was somewhat smaller than the majority. The contour could be measured with some certainty to  $\frac{1}{10}$  of a millimetre, by placing a scale along any required distance and observing through a magnifying lens. The true, or "normal" breadth is, by the preceding section, the apparent breadth on the distorted curve, and is denoted by 2x. The height above a fixed base line is y. The following were the values of x and y for arbitrarily selected points:—

$\mathrm{m}\mathrm{m}.$	mm.	mm.	mm.
2.e = 0.0,	y = 13.2,	2x = 4.0,	y = 10.0,
2x = 2.8,	y = 11.8,	2x = 4.4,	y = 9.4,
2x = 3.4,	y = 11.0,	2x = 4.7	y = 8.6.

The total change of height between two orders distant 88.5 mm. was 11.4 mm., giving a rate 11.4/88.5 per mm. The contour should, therefore, possess the equation,

$$-kx^2 = y - h - \frac{11.4x}{88.5},$$

and calculating from the second and fifth values of corresponding co-ordinates in the above list, we find,

$$k = 0.847$$
,  $h = 13.3$  mm.

The calculated height is therefore 13.3 against the measured value 13.2, so that the result is accurate to 1 part in 130. With y = 8.6, we find by calculation, x = 2.38 against the observed value 2.35. The other values are reproduced with similar accuracy, and we conclude that the undistorted curve is strictly parabolic, and that the probability distribution of intensity is correct for the case of the Hydrogen lines in the ordinary discharge. The intensity at a distance  $\lambda - \lambda_0$  from the maximum at  $\lambda_0$  is proportional to  $\exp(-k^2(\lambda - \lambda_0)^2)$  where  $k^2$  is some constant. The plate to which the above typical calculation relates is, in fact, much smaller than the others, so that the accuracy there obtained is a minimum. It is much greater in the calculations from the other plates, and we may, therefore, conclude that calculated distances are only subject to a possible error of about 1 part in 100 at most, and an error even less if the mean of several calculations is taken. The material is, therefore, at hand for a very accurate determination of the separation in  $H_a$  and  $H_{\beta}$ .

The actual plates were taken slightly out of focus, in order to remove the trouble caused by the grain of the plate. The exactness of the parabolic forms which the

normal contours take removes the necessity for giving a detailed investigation of the effect of this procedure. It is evident that, as could be proved otherwise, it introduces no appreciable change in the distances between axes of parabolas.

The photograph for  $H_a$  is found to consist of two parabolas—slightly distorted—as

in the figure (fig. 6), where the normal parabolas are shown, intersecting at P. The axes are  $a_1$  and  $a_2$  and  $\sigma$ is their separation on the photograph whose contour is APBC. Near P, of course, since intensities are additive, the parabolic forms are lost, and points close to P should not be selected for measurement. Calculation shows that this region round P is, in fact, nearly negligible, but we do not exhibit the calculation, for it is somewhat The equation for the parabolic form above P can be found with accuracy as in the last section for the distorted or normal curve. It is convenient to use the latter. We can then calculate the half breadth x

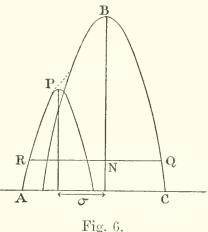


Fig. 6.

of the normal curve at Q, and thence the apparent one x' by the formula

$$x' = x - \frac{\alpha x^2}{2d_0^2}.$$

The whole breadth QR of the contour may be measured, and thence the apparent RN in the figure, equal to x''. This can be reduced to the normal value x (say), which is  $\sigma + X$ , where  $\sigma$  is the separation and X the co-ordinate of R relative to the axis of its own parabola. By finding X and the heights for various points,  $\sigma$  may be deduced and thence δλ. There is, however, a simpler method of procedure. The axis of the upper parabola, when made normal in the longitudinal direction, is the locus of the central points of the various breadths, and can be drawn on the curve. Since Rayleigh's theory has been shown by a direct method to be applicable to these experiments, we may at once assume that  $k^2$  in the law of intensity is the same for both components of  $H_a$ . The equations of the separate parabolas, with reference to the axis of y just constructed, should therefore be

$$k\hat{\xi}^2 = h_1 - y + \beta \hat{\xi},$$
  
$$k(\hat{\xi} - \sigma)^2 = h_2 - y + \beta \hat{\xi},$$

where  $h_1$  and  $h_2$  are their heights, and  $\beta$  is the rate of change of height of the maxima per millimetre. For the same height y, if  $\xi_1$  and  $\xi'_1$  are two abscissæ,

$$k\{\hat{\xi}_1^2 - (\hat{\xi}'_1 - \sigma)^2\} = h_1 - h_2 + \beta(\hat{\xi}_1 - \hat{\xi}'_1)$$

and for two other abscisse  $\hat{\xi}_2$ ,  $\hat{\xi}'_2$ , measured on the normal scale,

$$k\{\xi_2^2 - (\xi'_2 - \sigma)^2\} = h_1 - h_2 + \beta(\xi_2 - \xi'_2),$$

and, by subtraction,  $h_1-h_2$  is eliminated. Investigation shows at once, as in the following numerical examples, that the term in  $\beta$  in the result of this subtraction cannot affect even the third decimal place in the calculated separation and we may, therefore, omit it at once.

Thus finally,

$$\sigma = (\xi_1'^2 - \xi_1^2 - \xi_2'^2 + \xi_2^2)/2(\xi_1' - \xi_2'^2).$$

These magnitudes  $\xi$  are true normal breadths, deduced from the observed values by correction for dispersion.

In a series of fringes for  $H_a$ , the intervals between one fringe and its neighbours on either side were 14.0, 15.3 mm., and the next interval in the direction in which they decrease was 12.7. The law of maxima stated already is fulfilled, for these numbers are in arithmetical progression. The appropriate normal separation for the fringe in question, now the subject of examination, is the mean of 14.0 and 15.3, or 14.66. In other words, a separation 14.66 mm. corresponds to the interval  $\delta\lambda = \epsilon = 0.4301$  Å.U. for  $H_a$ . Moreover,  $\alpha = 1.3$ ,  $d_0 = 2(14.0) - 15.3 = 12.7$ .

A real normal breadth  $\xi$  on the right of the axis of the main component indicates, therefore, an apparent breadth x, where

$$x = \xi - \frac{\alpha \xi^2}{2d_0^2} = \xi - 0.0048 \xi^2, \qquad \xi = x + 0.0048 x^2,$$

and the same breadth  $\xi$  on on the left, an apparent breadth x' where

$$x' = \hat{\xi} + 0.0048\hat{\xi}^2, \qquad \hat{\xi} = x' + 0.0048x'^2.$$

We can also calculate the real breadths on the right from the equation to the parabola for the main component. Actual measurements of the total breadths at the points  $y = 19^{\circ}4$  cm.,  $y = 16^{\circ}5$  cm. give  $2\xi = 4^{\circ}3$ ,  $2\xi = 6^{\circ}4$  respectively. These are points which depend only on the main component. The corresponding equation of the main parabola becomes

$$\hat{\xi}^2 = 1.969 (22.0 + 0.1 \hat{\xi} + y),$$

when the coefficient 0.1 is calculated. It agrees completely with the value derived by comparison with neighbouring fringes, which is 0.105, and the whole interpretation of the curves is justified. At the heights y = 12.8 cm., y = 11.0 cm., we thus find directly from the equation,

$$\hat{\xi}_1 = 4.355 \,\mathrm{mm.}, \qquad \hat{\xi}_2 = 4.753 \,\mathrm{mm.},$$

and when these are corrected to apparent breadths, the results agree with observation to one-tenth of a millimetre—the observations giving the apparent breadths on the right of the main axis.

The breadths on the left, when measured and corrected to normal dispersion, become

$$\xi'_1 = 5.49 \text{ mm.}$$
, corresponding to  $y = 12.8$ ,  $\xi_1 = 4.35$ ,

$$\hat{\xi}'_2 = 6.17 \text{ mm.}, \qquad y = 11.0, \quad \hat{\xi}_2 = 4.75.$$

Thus

$$\sigma = \{(5.49)^2 - (4.35)^2 - (6.17)^2 + (4.75)^2\} / 2(5.49 - 6.17),$$

or, on reduction,  $\sigma = 4.53$  mm. But 14.66 mm. corresponds to  $\delta \lambda = \epsilon = 0.4301$  Å.U., and the separation in wave-length is therefore

$$\delta \lambda = (4.53 \times 0.430)/14.66 = 0.133 \text{ Å.U.},$$

which is very close to Buisson and Fabry's value 0.132 Å.U. Three determinations have been made in this way, by the selection of different heights, and the others give values  $\delta\lambda = 0.130$ ,  $\delta\lambda = 0.134$  Å.U., the general mean being 0.1323 A.U. Buisson and Fabry's value is thus confirmed in an absolute manner, even to the third significant figure.

We found it necessary to avoid points too near the base of the photograph, where the successive fringes tended to merge into one another by the increase in breadth of the parabolas. It was impossible on this account to test the possible existence of a third component as given by Sommerfeld's theory. Its separation would only be 0.01, and its intensity as calculated by Sommerfeld\* would necessitate the appearance of its maximum in this particular region.

(XVIII.) The Structure of 
$$H_{\beta}$$
.

 $H_{\beta}$  is also broadened symmetrically in the normal spectrum, and follows the probability law of intensity with extreme accuracy. The following are details of a typical calculation of its upper portion—representing the main component—made from a larger plate than that quoted for  $H_{\alpha}$ .

For this plate,  $\alpha = 0.5$  mm.,  $d_0 = 9.75$  mm., and the rate of change of height of the maxima per millimetre = 0.111 mm. The height of the curve being  $h_1$ , its equation when corrected longitudinally should become

$$-kx^2 = y - h_1 - 0.111x.$$

Co-ordinates measured were, in millimetres,

$$2x = 3.4, 5.3, 6.7, 7.6,$$
  
 $y = 14.0, 11.9, 9.8, 8.0,$   
\* Loc. cit.

and calculating the constants k and  $h_1$  from the first and last, the equation becomes

$$0.5394x^2 = 15.368 + 0.111x - y$$
.

When x = 2.65, 3.35, we find y = 11.9, 9.7, by calculation from this formula, against the observed values 11.9, 9.8. The agreement is almost exact, and the stronger component of  $H_{\beta}$  follows the same law as that of  $H_{\alpha}$ . It is, moreover, evident that the error of measurement in x cannot exceed about one-tenth of a millimetre at any point, and we may credit, therefore, the final separation of the components on the plate with this rough degree of accuracy. The scale of the plate being, as stated above, 9.5 mm. for a separation  $\epsilon$ , equal to 0.22, the error in the deduced separation could be as great as  $(0.1 \times 0.22)/9.75 = 0.002$  Å.U., but this should be practically the limit of error in any individual determination.

A simple inspection of the photographs indicates that there can be no second component of  $H_{\beta}$  with a separation comparable to that in  $H_{\alpha}$ . If the series  $H_{\alpha}$ ,  $H_{\beta}$ , ... is Diffuse or Sharp, the separation in  $H_{\beta}$  should be 0.07 Å.U., and if it is Principal, 0.03 Å.U., according to a preceding calculation. The second component which can actually be seen on the photographs does not at first sight appear likely to lead to the former value, and accurate measurements show that the latter is the true value. A typical calculation is as follows:—

At one definite height, the breadths of the pattern on the right and left of the centre were  $x_1 = 3.9$ ,  $x_2 = 4.3$ , and at another height  $x'_1 = 4.4$ ,  $x'_2 = 5.0$ , the points being selected away from the junction of the curves. The true breadths on the normal scale are, if  $\beta = \alpha/d_0^2$ ,

$$\xi_1 = 3.9 (1 + 1.95\beta), \qquad \xi'_1 = 4.3 (1 - 2.15\beta), 
\xi_2 = 4.4 (1 + 2.2\beta), \qquad \xi'_2 = 5.0 (1 - 2.5\beta),$$

and neglecting, as is legitimate, the effect of the correction for height, the separation  $\sigma$  is given by

$$\sigma = (\xi_1'^2 + \hat{\xi}_1^2 - \hat{\xi}_2'^2 + \hat{\xi}_2^2)/2 (\hat{\xi}_1' - \hat{\xi}_2'),$$

which becomes, to order  $\beta$ 

$$\sigma = (2.36 - 71\beta)/(1.4 - 6.5\beta).$$

But for this plate,  $\beta = 0.5/(9.75)^2 = 0.0053$ , and finally  $\sigma = 1.98/1.37 = 1.44$  mm. But on the plate, 9.75 mm. corresponds to  $\delta\lambda = \epsilon = 0.23$  Å.U., and  $\sigma$  thus corresponds to  $\delta\lambda = 0.033$  Å.U., which is the separation in H<sub>\beta</sub>.

There is thus no doubt that the Balmer series is a Principal series. The limit of error to be expected in the results, as above, is roughly 0.002 Å.U., and the true separation for a Principal series is 0.030 Å.U., so that the result is within the limit of error. Not only, therefore, can the method be applied to the elucidation of the nature of this series, but it can separate lines whose interval is only 0.010 Å.U., or less with

precision, although such lines cannot be seen as resolved on account of their width. Even when the correction involving  $\beta$  is not applied, so that account is not taken of the variation of dispersion within the small breadth of the line, the result is  $\delta\lambda = 0.039 \,\text{Å}$ . U. This would be sufficient to indicate that there was no Diffuse series component, and it gives an estimate of the comparatively small degree of dependence of the result on irregularity of dispersion.

#### (XIX.) Discussion.

We may at once state that we have at present no theory to offer for the results obtained, but it would appear that the changes in relative intensity which we have found are facts which must be seriously considered in theories of the origin of spectra in relation to the structure of the atom. It cannot be said that spectroscopy has already passed from the descriptive to the rational state. We do not propose to discuss in detail the bearing of our results on the application of the quantum theory to the origin of spectra, but attention may be drawn to certain considerations. It would appear from the well-known relation  $Ve = h\nu$  that the distribution of intensity in a spectrum should be a simple function of the distribution of velocity among the electrons in the discharge tube, but this view appears to be negatived by the fact that different series behave in different ways, and we may probably conclude from this that the range of velocities of the electrons is not the sole factor which determines the emission in line spectra; this view appears to be strengthened by such phenomena as the apparently anomalous effect of Neon on the distribution of intensity in the Balmer series.\*

As regards the Balmer series, the separations of the components which we have found indicate that it is of the Principal type, and lend no direct support to the theoretical considerations advanced by Sommerfeld. In any case it can no longer be regarded as a Diffuse or Sharp series.

We do not venture to speculate further on the results we have obtained, which can only be regarded as preliminary in their scope, but we hope that the methods of investigation which we have outlined may lead to the detailed knowledge which must be essential to the further elucidation of spectrum series.

# (XX.) Summary.

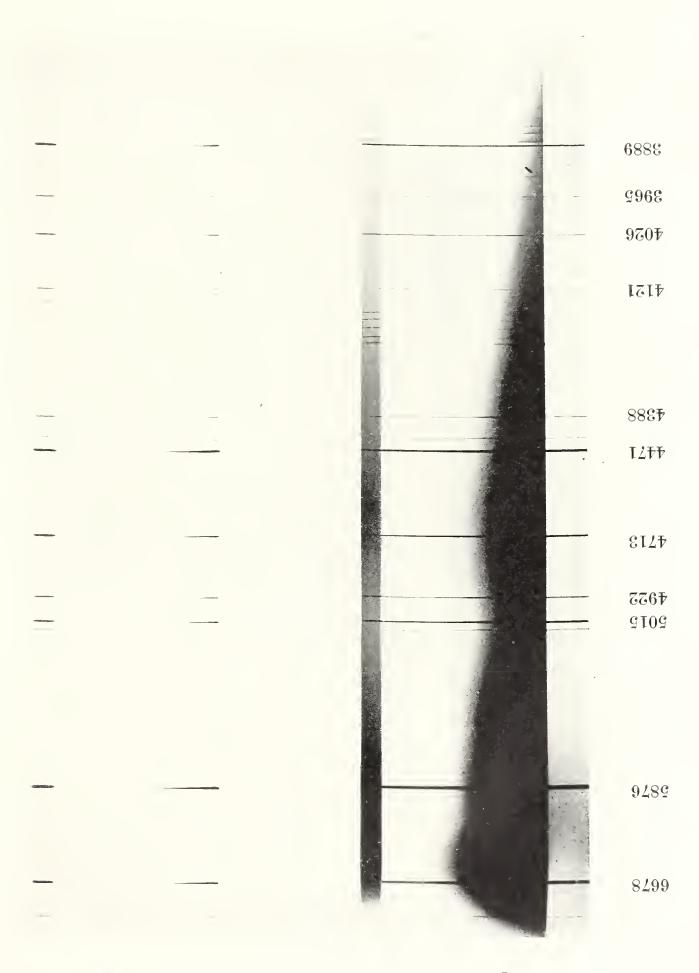
- 1. A method has been found for the accurate determination of the photographic intensities of spectrum lines, and the reduction of such intensities to absolute values by comparison with the continuous black body radiation of the Carbon arc.
- \* The remarks already made in a previous communication (loc. cit.) as to the sources of error attaching to photographic estimates of intensity appear to be applicable to some results obtained by RAU ('Sitz. Phys. Med. Ges. Wurtzburg,' February, 1914), whose conclusions appear to imply that a critical voltage, related to the frequency, is necessary to produce spectrum lines.

- 2. A study has been made of the relative intensity distribution in the spectra of Helium and Hydrogen under different conditions of excitation.
- 3. It has been found that under certain specified conditions there is a transfer of energy from the longer to the shorter wave-lengths in any given series, and that under such conditions the associated series, and in particular the Diffuse series, are relatively enhanced at the expense of the Principal series.
- 4. It has also been found that the distribution of intensity found in certain celestial spectra can be approximately reproduced in the laboratory.
- 5. A study has been made of the separations of the components of lines of the Balmer series of Hydrogen, and the mean values of the separations of the doublets constituting the lines  $H_{\alpha}$  and  $H_{\beta}$  have been found to be respectively 0.132 Å.U., and 0.033 Å.U. These values are consistent with the separations appropriate to Principal series, and the first is in precise agreement with the value deduced by Buisson and Fabry.

Note on the Band Spectrum of Helium.—We have made a number of observations of the pinkish glow which surrounds the cathode in a Helium tube excited by the ordinary discharge. The cathode glow in Helium presents a very striking appearance when viewed through coloured screens which transmit only a narrow region of the spectrum. Through a violet screen the dark space around the electrode is clearly defined and surrounded by a uniform glow. Viewed through a screen which transmits red rays only, the appearance is entirely changed, the "dark space" being in fact the region in which the red rays are predominant. The band spectrum of Helium is relatively strong in the cathode glow, though not intrinsically so strong as with the "bulb discharge."\* In this connection we may mention that we have definite evidence from the relative intensities of the bands in the "bulb discharge" and the cathode glow that this spectrum is capable of sub-division. Apart from theoretical considerations, this circumstance may be of importance in modifying the conclusion that the spectrum in question is absent from celestial spectra.

\* Curtis, 'Roy. Soc. Proc.,' A, vol. 89, p. 146, 1913.





B. Helium Ordinary Discharge

A. + Crater of Carbon Arc.



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Helium (bulb).

Helium (capacity).

Helium (ordinary discharge).



i i

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SERIES A, Vol. 217. Pp. 279-314.



# NUMERICAL RESULTS OF THE THEORY OF THE DIFFRACTION OF A PLANE ELECTROMAGNETIC WAVE BY A PERFECTLY CONDUCTING SPHERE.

BY

J. PROUDMAN, A. T. DOODSON, AND G. KENNEDY.

#### LONDON:

PUBLISHED BY THE ROYAL SOCIETY,

AND SOLD BY HARRISON AND SONS, ST. MARTIN'S LANE, W.C.,

Printers in Ordinary to His Majesty.

1917.

A 556.

#### PUBLISHED BY THE ROYAL SOCIETY,

BURLINGTON HOUSE, LONDON.

SOLD BY HARRISON AND SONS, St. MARTIN'S LANE.

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## VIII. Numerical Results of the Theory of the Diffraction of a Plane Electromagnetic Wave by a Perfectly Conducting Sphere.

By J. Proudman, A. T. Doodson, and G. Kennedy.

Communicated by T. J. I'A. Bromwich, Sc.D., F.R.S.

Received April 13,—Read November 23, 1916.

#### Introduction.

#### (By J. PROUDMAN.)

1. At the suggestion of Dr. Bromwich, I began the computations leading to this paper nearly three years ago. Using tables constructed by Lord Rayleigh\* and Prof. A. Lodge,\* I obtained results for  $\kappa a = 1, 2, 10^{\dagger}$  and  $\theta = 0^{\circ}$ ,  $180^{\circ}$ ;  $90^{\circ}$ ;  $45^{\circ}$ ,  $135^{\circ}$ ;  $20^{\circ}$ ,  $160^{\circ}$ ;  $70^{\circ}$ ,  $110^{\circ}$ ; in this order. From the results for  $\kappa a = 1$  and 2, graphs of  $Y_1, Y_2, Z_1, Z_2$  could be constructed with some confidence, but such graphs were entirely impossible in the case of  $\kappa a = 10$ , owing to the large number of their undulations. (For the graphs of these functions, as finally drawn, see figs. 1, 3, 18, 20, 22, 24.)

I then handed over the work to Messrs. Doodson and Kennedy, and the whole of the results as they now appear are due to them. Mr. Doodson first constructed tables; for Bessel's functions of half-integral orders, and Mr. Kennedy constructed tables, for the derivatives of Legendre's functions. These two sets of tables, together with those of Lodge already quoted, are what have been used in all the subsequent work.

Mr. Doodson computed quite independently the cases of  $\kappa a = 1, 2$ , for all the values of  $\theta$  that I had taken together with  $\theta = 10^{\circ}$ ,  $170^{\circ}$ ;  $30^{\circ}$ ,  $150^{\circ}$ ;  $60^{\circ}$ ,  $120^{\circ}$ ;  $80^{\circ}$ ,  $100^{\circ}$ . His results were in agreement with mine, except for a number of small differences

RAYLEIGH, "Incidence of Light upon a Transparent Sphere of Dimensions comparable with a Wavelength," 'Roy. Soc. Proc.,' A, vol. lxxxiv., p. 25 (1910); ['Sc. Papers,' vol. v., p. 547].

- † The notation is explained in the next section.
- † These have been published by the British Association; 'Report' for 1914, p. 87.
- § These are to be presented shortly to the British Association.

<sup>\*</sup> RAYLEIGH, "On the Acoustic Shadow of a Sphere, with an Appendix giving the Values of Legendre's Functions, . . ., by Prof. A. Lodge," 'Phil. Trans. Roy. Soc.,' A, vol. cciii., p. 87 (1904); ['Sc. Papers,' vol. v., p. 149].

which he found to be due to numerical errors on my part. From the larger number of values of  $\theta$  thus taken, graphs of  $Y_1^2 + Y_2^2$ ,  $Z_1^2 + Z_2^2$  (figs. 2, 4) could be constructed with confidence and no further work was necessary for  $\kappa a = 1, 2$ . Tables X., XI. ( $\kappa a = 1, 2$ ), and figs. 1 to 4, contain the results of this part of Mr. Doodson's work.

Sharing equally the labour, Messrs. Doodson and Kennedy then similarly recomputed the case of  $\kappa a = 10$ , and added the extra values of  $\theta$  which had been taken for  $\kappa a = 1, 2$ . It then proved possible to construct rough graphs of  $Y_1, Y_2, Z_1, Z_2$ , but the uncertainties in the graphs of  $Y_1^2 + Y_2^2, Z_1^2 + Z_2^2$  were very great, owing to the magnification of errors involved in the squaring. In order to get more insight into the general nature of the results, they performed for  $\kappa a = 9$  all the work that they had done for  $\kappa a = 10$ , sharing it similarly. The construction of accurate graphs of  $Y_1^2 + Y_2^2, Z_1^2 + Z_2^2$  proved as impossible as before, i.e., knowing only the points on the curves of figs. 25 to 28, indicated by small circles, the complete curves could not be drawn.

Mr. Doodson then conceived the idea of calculating the gradients of the curves at all the values of  $\theta$  taken, and formed the necessary series. Mr. Kennedy shared the computations with him, and the gradients were calculated at every known point of the curves for both  $\kappa a = 9$  and 10. These proved a great help.

At this stage the results obtained for  $\kappa a = 9$ , 10 were those indicated by the small circles and tangents in figs. 17 to 28. The small uncertainties in the graphs of  $Y_1, Y_2, Z_1, Z_2$ , still led to considerable uncertainties in those of  $Y_1^2 + Y_2^2, Z_1^2 + Z_2^2$ . Mr. Doodson then designed and carried out an examination of the way in which the results found differ from those given by the theoretical first approximation for large values of  $\kappa a$ . The sections on analysis of results and interpolation give this work. Some of the methods proved their utility by leading to the detection of certain errors in the previous work, and all of them were used for interpolation purposes in constructing the final curves.

Only the curves, as finally constructed from all considerations, are now given.

In the work of drawing up the results, all the curves have been drawn by Mr. Doodson, while most of the tables have been written out by Mr. Kennedy. Only a selection, however, is printed; the remainder are in the possession of the Royal Society. For instance, Tables I. to VIII. are only printed in so far as they refer to  $\kappa a = 10$ , while Tables XII. to XIX. which refer to the gradients, are somitted altogether.

#### General Formulæ.

- 2. For the theory of the problem we shall quote a paper by Dr. Bromwich on "The Scattering of Plane Waves by Spheres."\*
  - \* This is a paper which Dr. Bromwich communicated to the Society at the same time as the present one.

Using spherical polar co-ordinates r,  $\theta$ ,  $\phi$ , the incident plane wave train is taken to contain the time factor  $e^{i\kappa ct}$ , to travel along the negative direction of the axis  $\theta = 0$ , to be polarized in the plane  $\phi = \frac{1}{2}\pi$ , and to have the electric force of unit amplitude. The components of electric and magnetic force, in the disturbance produced by the sphere, along the directions of r,  $\theta$ ,  $\phi$  increasing, are denoted respectively by X, Y, Z and  $\alpha$ ,  $\beta$ ,  $\gamma$ . Then at a distance from the sphere, which is large compared with a wave-length of the incident train, we have, from the paper quoted,

$$X = c\alpha = 0,$$

$$Y = c\gamma = \frac{\partial M}{\partial \theta} - \frac{\partial N}{\sin \theta \partial \phi},$$

$$Z = -c\beta = \frac{\partial M}{\sin \theta \partial \phi} + \frac{\partial N}{\partial \theta},$$
(1)

where

$$M = \cos \phi \frac{e^{-i\kappa(r-ct)}}{\kappa r} \sin \theta \sum_{n=1}^{\infty} (-1)^{n+1} \frac{2n+1}{n(n+1)} \frac{S'_n(\kappa a)}{E'_n(\kappa a)} P'_n(\cos \theta),$$

$$N = \sin^{\dagger} \phi \frac{e^{-i\kappa(r-ct)}}{\kappa r} \sin \theta \sum_{n=1}^{\infty} (-1)^{n+1} \frac{2n+1}{n(n+1)} \frac{S_n(\kappa a)}{E_n(\kappa a)} P'_n(\cos \theta).$$
(2)

Take now

$$Y = \cos \phi \frac{e^{-i\kappa(r-ct)}}{\kappa r} (Y_1 + iY_2),$$

$$Z = \sin \phi \frac{e^{-i\kappa(r-ct)}}{\kappa r} (Z_1 + iZ_2),$$
(3)

where Y<sub>1</sub>, Y<sub>2</sub>, Z<sub>1</sub>, Z<sub>2</sub> are real. Then the time-means of the squares of the real parts of Y and Z are respectively

$$\frac{1}{2} \frac{\cos^2 \phi}{(\kappa r)^2} (Y_1^2 + Y_2^2), \qquad \frac{1}{2} \frac{\sin^2 \phi}{(\kappa r)^2} (Z_1^2 + Z_2^2). \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

These give a measure of the energy of the disturbance.

The functions  $Y_1$ ,  $Y_2$ ,  $Z_1$ ,  $Z_2$  involve only  $\kappa a$  and  $\theta$ . It is the object of the present paper to evaluate them, together with  $Y_1^2 + Y_2^2$  and  $Z_1^2 + Z_2^2$  for certain values of  $\kappa \alpha$ , and all values of  $\theta$  from 0 to  $\pi$ .

Writing  $\cos \theta = \mu$ , we have

$$\frac{d}{d\theta} \left\{ \sin \theta \mathbf{P}'_{n}(\mu) \right\} = n (n+1) \mathbf{P}_{n}(\mu) - \mu \mathbf{P}'_{n}(\mu),$$

using which we obtain

$$Y_1 = A + \mu A' - C',$$
  $Y_2 = B + \mu B' - D',$   $Z_1 = A' + \mu A - C,$   $Z_2 = B' + \mu B - D,$   $Z_3 = B' + \mu B - D,$  (5)

where

$$A = \sum_{n=1}^{\infty} (-1)^{n} \frac{2n+1}{n(n+1)} \frac{S_{n}(\kappa a) C_{n}(\kappa a)}{|E_{n}(\kappa a)|^{2}} P'_{n}(\mu),$$

$$B = \sum_{n=1}^{\infty} (-1)^{n} \frac{2n+1}{n(n+1)} \frac{S_{n}^{2}(\kappa a)}{|E_{n}(\kappa a)|^{2}} P'_{n}(\mu),$$

$$C = \sum_{n=1}^{\infty} (-1)^{n} (2n+1) \frac{S_{n}(\kappa a) C_{n}(\kappa a)}{|E_{n}(\kappa a)|^{2}} P_{n}(\mu),$$

$$D = \sum_{n=1}^{\infty} (-1)^{n} (2n+1) \frac{S_{n}^{2}(\kappa a)}{|E_{n}(\kappa a)|^{2}} P_{n}(\mu),$$

$$(6)$$

and

$$A' = \sum_{n=1}^{\infty} (-1)^{n} \frac{2n+1}{n(n+1)} \frac{S'_{n}(\kappa a) C'_{n}(\kappa a)}{|E'_{n}(\kappa a)|^{2}} P'_{n}(\mu),$$

$$B' = \sum_{n=1}^{\infty} (-1)^{n} \frac{2n+1}{n(n+1)} \frac{S'_{n}^{2}(\kappa a)}{|E'_{n}(\kappa a)|^{2}} P'_{n}(\mu),$$

$$C' = \sum_{n=1}^{\infty} (-1)^{n} (2n+1) \frac{S'_{n}(\kappa a) C'_{n}(\kappa a)}{|E'_{n}(\kappa a)|^{2}} P_{n}(\mu),$$

$$D' = \sum_{n=1}^{\infty} (-1)^{n} (2n+1) \frac{S'_{n}^{2}(\kappa a)}{|E'_{n}(\kappa a)|^{2}} P_{n}(\mu).$$

$$(7)$$

Further, we easily obtain

$$\frac{\partial Y_{1}}{\partial \mu} = \frac{\mu Y_{1} + Z_{1}}{1 - \mu^{2}} - \frac{\partial C'}{\partial \mu}, \qquad \frac{\partial Y_{2}}{\partial \mu} = \frac{\mu Y_{2} + Z_{2}}{1 - \mu^{2}} - \frac{\partial D'}{\partial \mu}, 
\frac{\partial Z_{1}}{\partial \mu} = \frac{\mu Z_{1} + Y_{1}}{1 - \mu^{2}} - \frac{\partial C}{\partial \mu}, \qquad \frac{\partial Z_{2}}{\partial \mu} = \frac{\mu Z_{2} + Y_{2}}{1 - \mu^{2}} - \frac{\partial D}{\partial \mu},$$
(8)

while if we denote  $\partial C/\partial \mu$ ,  $\partial D/\partial \mu$ ,  $\partial C'/\partial \mu$ ,  $\partial D'/\partial \mu$  by c, d, c', d' respectively, we have

$$c = \sum_{n=1}^{\infty} (-1)^{n} (2n+1) \frac{S_{n} (\kappa a) C_{n} (\kappa a)}{|E_{n} (\kappa a)|^{2}} P'_{n} (\mu),$$

$$d = \sum_{n=1}^{\infty} (-1)^{n} (2n+1) \frac{S_{n}^{2} (\kappa a)}{|E_{n} (\kappa a)|^{2}} P'_{n} (\mu),$$

$$c' = \sum_{n=1}^{\infty} (-1)^{n} (2n+1) \frac{S'_{n} (\kappa a) C'_{n} (\kappa a)}{|E'_{n} (\kappa a)|^{2}} P'_{n} (\mu),$$

$$d' = \sum_{n=1}^{\infty} (-1)^{n} (2n+1) \frac{S'_{n}^{2} (\kappa a)}{|E'_{n} (\kappa a)|^{2}} P'_{n} (\mu).$$
(9)

In summing the series in (6), (7), (9), supplementing values of  $\theta$  may be considered at the same time if the odd and even terms of these series are taken separately. We

shall use the suffixes 1, 2, to denote respectively the sums of odd terms and sums of even terms. Then for supplementary values of  $\theta$ , the two values of each of

$$A_1, B_1, A'_1, B'_1, C_2, D_2, C'_2, D'_2, c_1, d_1, c'_1, d'_1,$$

are equal, while the two values of each of

$$A_2$$
,  $B_2$ ,  $A'_2$ ,  $B'_2$ ,  $C_1$ ,  $D_1$ ,  $C'_1$ ,  $D'_1$ ,  $c_2$ ,  $d_2$ ,  $c'_2$ ,  $d'_2$ ,

are equal and opposite. For this reason in computing Y<sub>1</sub>, for example, we evaluate

$$A_1 + \mu A'_2 - C'_2$$
,  $A_2 + \mu A'_1 - C'_1$ ,

separately for  $0 \le \theta \le \frac{1}{2}\pi$ .

For  $\theta = 0$  we have

$$2P'_n(\mu) = n(n+1)P_n(\mu),$$

so that

$$C_1 = 2A_1$$
,  $D_1 = 2B_1$ ,  $C'_1 = 2A'_1$ ,  $D'_1 = 2B'_1$ ,

$$C_2 = 2A_2$$
,  $D_2 = 2B_2$ ,  $C'_2 = 2A'_2$ ,  $D'_2 = 2B'_2$ .

Numerical Summation of Series.

(By A. T. Doodson and G. Kennedy.)

3. The first step was to construct tables of

$$\log (2n+1) \operatorname{F}_{n}(\kappa \alpha)$$
 and  $\log \frac{2n+1}{n(n+1)} \operatorname{F}_{n}(\kappa \alpha)$ ,

where  $F_n(\kappa a)$  takes each of the forms

$$\frac{|S_n(\kappa \alpha) C_n(\kappa \alpha)|}{|E_n(\kappa \alpha)|^2}, \qquad \frac{|S_n^2(\kappa \alpha)|}{|E_n(\kappa \alpha)|^2}, \qquad \frac{|S_n'(\kappa \alpha) C_n'(\kappa \alpha)|}{|E_n(\kappa \alpha)|^2}, \qquad \frac{|S_n'(\kappa \alpha) C_n'(\kappa \alpha)|}{|E_n'(\kappa \alpha)|^2}.$$

This was done by means of the Brit. Assoc. tables\* mentioned in § 1, using seven-figure logarithms and afterwards reducing to five figures. To each of these was added  $\log |P_n(\mu)|$  or  $\log |P'_n(\mu)|$  for the same value of n, using five-figure logarithms.

<sup>\*</sup> In these tables the values of  $|E_n(9)|^2$  for n = 13, 14 are misprinted; the decimal point requires moving one place to the left in each case. Care should be taken in using the logarithms, as some of the negative characteristics are printed without the sign placed over them.

Checks were devised to secure accurate addition, and no errors were afterwards discovered in this part of the work.

Tables\* I. to VIII. were then constructed by taking anti-logarithms. This was a step the accuracy of which was not easily checked. The method used was to repeat the work with a different book of logarithms and under different conditions so as to avoid "repetition" errors. Only one or two errors were afterwards found in this part of the work. More errors were made in the summation of odd terms and of even terms of the series, the results of which are given at the feet of Tables I. to VIII. Only five or six, however, which escaped immediate detection by checking, were afterwards found in Table X. How these were detected will be described in the section on analysis of results. Except in the cases of  $\kappa a = 1, 2$ , one person computed A, B, C, D and the other A', B', C', D'. The final work of combining these functions was done separately by each and the results compared.

It has been the practice throughout the work to use more figures than were strictly necessary for the desired degree of accuracy. For example, many terms in the anti-logarithms are given to six figures, though only five-figure logarithms were used. This was found conducive to speed and accuracy, but it is not intended that the tables should be regarded as accurate to the extent given, except when this is stated.

The final results for  $Y_1$ ,  $Y_2$ ,  $Z_1$ ,  $Z_2$  are probably accurate to at least three decimal places, while  $Y_1^2 + Y_2^2$  and  $Z_1^2 + Z_2^2$  can safely be given to four significant figures, as is done in the tables.

The derivatives c', d', c, d were computed similarly. The gradients are probably accurate to the order given in the tables.†

<sup>\*</sup> The reason that  $\theta = 45^{\circ}$  has been taken where a regular sequence would require  $\theta = 40^{\circ}$ , 50°, appears from the account of the history of the work in § 1.

<sup>†</sup> As stated at the end of § 1, these are not printed. The unprinted tables referring to this section are as follows:—

TABLE I.

$$(-1)^n \cdot \frac{2n+1}{n(n+1)} \cdot \frac{S_n C_n}{|E_n|^2} \cdot P'_n. \quad \kappa \alpha = 10.$$

n.	O°.	10°.	20°.	30°.	45°.	60°.	70°.	80°.	90°.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17	$+1 \cdot 22990$ $+1 \cdot 23766$ $-0 \cdot 07073$ $-2 \cdot 41068$	$\begin{array}{c} +1 \cdot 21121 \\ +1 \cdot 19102 \\ -0 \cdot 06598 \\ -2 \cdot 16202 \\ -1 \cdot 99807 \\ +1 \cdot 99072 \\ +1 \cdot 89911 \end{array}$	-1.16415 + 0.90966	$ \begin{vmatrix} +1.06512 \\ +0.85088 \\ -0.03445 \\ -0.69684 \\ -0.26883 \\ -0.04634 \\ -0.26095 \\ +0.65908 \\ -0.46030 \\ +0.15650 \\ -0.02496 \\ -0.00058 \\ +0.00115 \end{vmatrix} $	$\begin{array}{c} + 0.86968 \\ + 0.46412 \\ - 0.00625 \\ + 0.22600 \\ + 0.36153 \\ - 0.29371 \\ - 0.09373 \\ - 0.18202 \\ + 0.25607 \\ - 0.10103 \\ + 0.00156 \\ + 0.00296 \\ - 0.00118 \\ + 0.00017 \end{array}$	$\begin{array}{c} + 0 \cdot 07735 \\ + 0 \cdot 01105 \\ + 0 \cdot 35783 \\ + 0 \cdot 06391 \\ + 0 \cdot 17394 \\ + 0 \cdot 19362 \\ - 0 \cdot 07589 \\ - 0 \cdot 14533 \\ + 0 \cdot 07855 \\ - 0 \cdot 00581 \end{array}$	+0.42065 $-0.12844$ $+0.01319$ $+0.10557$ $-0.19408$ $+0.18124$ $-0.03380$ $+0.27973$ $-0.08707$ $-0.04713$ $+0.01987$ $+0.00005$ $-0.00078$ $+0.00008$	$\begin{array}{c} + 0.73176 \\ + 0.21357 \\ - 0.26277 \\ + 0.00856 \\ - 0.17988 \\ - 0.20929 \\ - 0.05268 \\ - 0.16560 \\ + 0.02119 \\ + 0.16063 \\ - 0.02813 \\ - 0.01627 \\ + 0.00310 \\ + 0.00045 \\ - 0.00010 \end{array}$	$\begin{array}{c} + 0.73176 \\ 0.00000 \\ - 0.30941 \\ 0.00000 \\ - 0.30134 \\ 0.00000 \\ - 0.19259 \\ 0.00000 \\ - 0.25805 \\ 0.00000 \\ + 0.06585 \\ 0.00000 \\ - 0.0430 \\ 0.00000 \\ + 0.00011 \end{array}$
 $egin{array}{c} \mathbf{A}_1 \ \mathbf{A}_2 \end{array}$		-2.54161 + 3.54231	+ 0 · 62811 + 0 · 64101			+1:33968 +0:73328		+0:23249 -0:00795	$\begin{array}{c} -0.26797 \\ 0.00000 \end{array}$

TABLE II.

$$(-1)^n \cdot \frac{2n+1}{n(n+1)} \cdot \frac{S_n^2}{|E_n|^2} \cdot P'_n$$
.  $\kappa \alpha = 10$ .

				(, -)	1 12 1				
n.	0°.	10°.	20°.	30°.	45°.	60°.	70°.	80°.	90°.
2 3 4	- 0.91441 + 1.47323 - 0.51278 + 4.49904 - 4.42676 + 0.99175 - 6.57582 + 7.67697 - 4.20186 + 1.29223 - 0.22869 + 0.02289 - 0.00132 + 0.00001	- 0.91441 + 1.45086 - 0.49346 + 4.19691 - 1.27959 + 0.84781 - 5.31019 + 5.80016 - 2.93968 + 0.82779 - 0.13248 + 0.01182 - 0.00060 + 0.00002		$\begin{array}{c} -0.91441 \\ +1.27585 \\ -0.35253 \\ +2.19164 \\ -0.41242 \\ +0.11407 \\ +0.12362 \\ -0.79697 \\ +0.58691 \\ -0.17244 \\ +0.02229 \\ -0.00107 \\ -0.00001 \end{array}$	$\begin{array}{c} -0.91441 \\ +1.04174 \\ -0.19229 \\ +0.39767 \\ +0.13376 \\ -0.15340 \\ +0.78345 \\ -0.28627 \\ -0.16208 \\ +0.09593 \\ -0.01439 \\ +0.00049 \\ +0.00003 \end{array}$	-0.46397 +0.59133 -0.06758 -0.05444 +0.01119		$\begin{array}{c} -0 \cdot 91441 \\ +0 \cdot 25583 \\ +0 \cdot 10887 \\ -0 \cdot 54472 \\ -0 \cdot 10646 \\ +0 \cdot 08881 \\ +0 \cdot 14051 \\ -0 \cdot 50578 \\ +0 \cdot 01887 \\ +0 \cdot 06018 \\ -0 \cdot 00401 \\ -0 \cdot 00070 \\ +0 \cdot 00003 \end{array}$	$ \begin{array}{c} 0.00000 \\ -0.17835 \\ 0.00000 \\ +0.51374 \\ 0.00000 \\ -0.22979 \\ 0.00000 \\ +0.00938 \\ 0.00000 \end{array} $
T	- 13 · 86164 + 15 · 95612	$ \begin{array}{c c} -11.07041 \\ +13.13537 \end{array} $	$-5 \cdot 22918 + 7 \cdot 17705$		-0.36593 + 1.09616	-1.25508 + 0.54315	-1.03977 -0.38787	- 0.75660 - 0.64638	-0:67127 0:00000

TABLE III.

$$(-1)^n \frac{2n+1}{n(n+1)} \cdot \frac{S'_n C'_n}{|E'_n|^2} \cdot P'_n$$
.  $\kappa \alpha = 10$ .

n.	o°.	10°.	20°.	30°.	45°.	60°.	70°.	80°.	90°.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17	$\begin{array}{c} -0.73208 \\ -1.22846 \\ -1.22031 \\ +0.13013 \\ +2.47053 \\ +2.14057 \\ -2.86418 \\ -1.41534 \\ +4.16121 \\ -4.59928 \\ +2.69718 \\ -0.79823 \\ +0.17486 \\ -0.03159 \\ +0.00479 \\ -0.00062 \\ +0.00007 \end{array}$	$\begin{array}{c} -0.73208 \\ -1.20979 \\ -1.17433 \\ +0.12139 \\ +2.21569 \\ +1.82991 \\ -2.31292 \\ -1.06933 \\ +2.91125 \\ -2.94625 \\ +1.56243 \\ -0.41233 \\ +0.07926 \\ -0.01233 \\ +0.00157 \\ -0.00017 \\ +0.00001 \end{array}$		$\begin{array}{c} -0.73208 \\ -1.06387 \\ -0.83896 \\ +0.06339 \\ +0.71413 \\ +0.24621 \\ +0.05384 \\ +0.14693 \\ -0.58123 \\ +0.61373 \\ -0.26291 \\ +0.03728 \\ +0.00076 \\ -0.00140 \\ +0.00032 \\ -0.00004 \end{array}$	$\begin{array}{c} -0.73208 \\ -0.86866 \\ -0.45761 \\ +0.01150 \\ -0.23161 \\ -0.33110 \\ +0.34124 \\ +0.05278 \\ +0.16052 \\ -0.34142 \\ +0.16973 \\ -0.01726 \\ -0.00387 \\ +0.00144 \\ -0.00019 \\ +0.00001 \end{array}$	$\begin{array}{c} -0.73208 \\ -0.61423 \\ -0.07627 \\ -0.02033 \\ -0.36672 \\ -0.05853 \\ -0.20209 \\ -0.10902 \\ +0.06692 \\ +0.19377 \\ -0.13196 \\ +0.00868 \\ +0.00502 \\ -0.00109 \\ +0.00004 \\ +0.00001 \end{array}$	$\begin{array}{c} -0.73208 \\ -0.42016 \\ +0.12664 \\ -0.02427 \\ -0.10819 \\ +0.17774 \\ -0.21057 \\ +0.01903 \\ -0.24669 \\ +0.11609 \\ +0.07918 \\ -0.02968 \\ -0.00006 \\ +0.00095 \\ -0.00009 \\ -0.00001 \end{array}$	$\begin{array}{c} -0.73208 \\ -0.21332 \\ +0.25908 \\ -0.01576 \\ +0.18434 \\ +0.19168 \\ +0.06120 \\ +0.09325 \\ -0.01869 \\ -0.21418 \\ +0.04725 \\ +0.02430 \\ -0.00406 \\ -0.00054 \\ +0.00012 \\ +0.00000 \end{array}$	$ \begin{array}{c} -0.73208 \\ 0.00000 \\ +0.30508 \\ 0.00000 \\ +0.30882 \\ 0.00000 \\ +0.22376 \\ 0.00000 \\ +0.22756 \\ 0.00000 \\ -0.11063 \\ 0.00000 \\ -0.11063 \\ 0.00000 \\ -0.00564 \\ 0.00000 \\ -0.00013 \\ 0.00000 \end{array} $
$egin{array}{c} A'_1 \ A'_2 \end{array}$	+4.69207	$+2.55088 \\ -3.69890$	-0.84279 -0.44396	$ \begin{array}{r} -1.64613 \\ +0.04223 \end{array} $	-0.75387 $-1.49271$	-1·43714 -0·60074	-1·09186 -0·16031	$ \begin{array}{r}  -0.20284 \\  -0.13457 \end{array} $	+ 0·22802 0·00000

Table IV.

$$(-1)^n \frac{2n+1}{n(n+1)} \cdot \frac{S'_n^2 P'_n}{|E'_n|^2} = \kappa a = 10.$$

n.	0°.	10°.	20°.	30°.	45°.	60°.	70°.	80°.	90°.
2 3 4 5 6 7 8 9	$\begin{array}{c} - & 0.58704 \\ + & 1.01895 \\ - & 3.00442 \\ + & 0.00376 \\ - & 3.95795 \\ + & 5.69547 \\ - & 1.32944 \\ + & 0.24259 \\ - & 2.45947 \\ + & 2.71838 \\ - & 0.67180 \\ + & 0.05118 \\ - & 0.00227 \\ + & 0.00007 \\ \end{array}$	$\begin{array}{c} + \ 1 \cdot 00346 \\ - \ 2 \cdot 89121 \\ + \ 0 \cdot 00351 \\ - \ 3 \cdot 54969 \\ + \ 4 \cdot 86889 \\ - \ 1 \cdot 07357 \\ + \ 0 \cdot 18329 \\ - \ 1 \cdot 72068 \\ + \ 1 \cdot 74137 \\ - \ 0 \cdot 38916 \\ + \ 0 \cdot 02644 \end{array}$	$ \begin{vmatrix} +0.95750 \\ -2.56513 \\ +0.00281 \\ -2.47965 \\ +2.83681 \\ -0.49057 \\ +0.05965 \\ -0.33071 \\ +0.10721 \\ +0.02418 \\ -0.00462 \end{vmatrix} $	$+0.88243 \\ -2.06552$	$\begin{array}{c} +0.72051 \\ -1.12665 \\ +0.00033 \\ +0.37106 \\ -0.88097 \\ +0.15839 \\ -0.00905 \\ -0.09487 \\ +0.20179 \\ -0.04227 \\ +0.00111 \end{array}$	$\begin{array}{c} -0.58704 \\ +0.50947 \\ -0.18778 \\ -0.00059 \\ +0.58750 \\ -0.15574 \\ -0.09380 \\ +0.01869 \\ -0.03955 \\ -0.11452 \\ +0.03287 \\ -0.00056 \\ -0.00007 \end{array}$	$\begin{array}{c} -0.58704 \\ +0.34850 \\ +0.31180 \\ -0.00070 \\ +0.17332 \\ +0.47292 \\ -0.09774 \\ -0.00326 \\ +0.14580 \\ -0.06862 \\ -0.01972 \\ +0.00190 \\ 0.00000 \end{array}$		$ \begin{array}{c} -0.58704 \\ 0.00000 \\ +0.75109 \\ 0.00000 \\ -0.49473 \\ 0.00000 \\ +0.10386 \\ 0.00000 \\ -0.13450 \\ 0.00000 \\ +0.02755 \\ 0.00000 \\ -0.00000 \\ -0.00000 \end{array} $
	-12.01239 + 9.73040					-0.28787 + 0.25675	-0.07358 + 0.75074	-0.21677 + 0.79553	-0·33384 0·00000

Table V.  $(-1)^n \cdot (2n+1) \cdot \frac{S_n C_n}{|E_n|^2} \cdot P_n$ .  $\kappa a = 10$ .

n.	o°.	10°.	20°.	30°.	45°.	60°.	70°.	80°.	90°.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17		$\begin{array}{c} +1\cdot 44129 \\ +2\cdot 34855 \\ +2\cdot 25393 \\ -0\cdot 12069 \\ -3\cdot 77990 \\ -3\cdot 29306 \\ +3\cdot 03927 \\ +2\cdot 62343 \\ -3\cdot 99003 \\ +2\cdot 21758 \\ -0\cdot 70633 \\ +0\cdot 12885 \\ -0\cdot 00675 \\ -0\cdot 00333 \\ +0\cdot 00120 \\ -0\cdot 00024 \\ +0\cdot 00003 \end{array}$	$\begin{array}{c} +1 \cdot 37528 \\ +2 \cdot 02820 \\ +1 \cdot 64581 \\ -0 \cdot 06719 \\ -1 \cdot 30897 \\ -0 \cdot 52867 \\ -1 \cdot 26605 \\ +3 \cdot 31902 \\ -2 \cdot 76834 \\ +1 \cdot 28484 \\ -0 \cdot 37711 \\ +0 \cdot 07160 \\ -0 \cdot 00826 \\ +0 \cdot 00031 \\ +0 \cdot 00009 \\ -0 \cdot 00002 \end{array}$	$\begin{array}{c} +1 \cdot 26745 \\ +1 \cdot 53738 \\ +0 \cdot 80388 \\ -0 \cdot 00332 \\ +1 \cdot 07647 \\ +1 \cdot 74840 \\ -2 \cdot 02232 \\ -1 \cdot 70310 \\ +1 \cdot 78904 \\ -0 \cdot 04856 \\ -0 \cdot 51602 \\ +0 \cdot 29199 \\ -0 \cdot 08184 \\ +0 \cdot 01347 \\ -0 \cdot 00121 \\ +0 \cdot 00000 \\ +0 \cdot 00002 \end{array}$	$\begin{array}{c} +1 \cdot 03488 \\ +0 \cdot 61495 \\ -0 \cdot 43759 \\ +0 \cdot 05747 \\ +1 \cdot 81113 \\ +0 \cdot 69388 \\ +0 \cdot 62644 \\ +1 \cdot 49982 \\ -2 \cdot 69464 \\ +0 \cdot 79415 \\ +0 \cdot 33453 \\ -0 \cdot 26368 \\ +0 \cdot 06388 \\ -0 \cdot 00507 \\ -0 \cdot 00075 \\ +0 \cdot 00024 \\ -0 \cdot 00003 \end{array}$	$\begin{array}{c} + 0 \cdot 73176 \\ - 0 \cdot 30748 \\ - 1 \cdot 08295 \\ + 0 \cdot 04089 \\ - 0 \cdot 43317 \\ - 1 \cdot 51102 \\ + 1 \cdot 10020 \\ - 0 \cdot 37020 \\ + 2 \cdot 52819 \\ - 1 \cdot 29858 \\ - 0 \cdot 20509 \\ + 0 \cdot 24983 \\ - 0 \cdot 04425 \\ - 0 \cdot 00298 \\ + 0 \cdot 00173 \\ - 0 \cdot 00016 \\ - 0 \cdot 00001 \end{array}$	$\begin{array}{c} + 0.50055 \\ - 0.79829 \\ - 1.02233 \\ + 0.00054 \\ - 1.58172 \\ - 0.97641 \\ - 0.73228 \\ - 1.39766 \\ + 0.44907 \\ + 1.51386 \\ - 0.59867 \\ - 0.08421 \\ + 0.05977 \\ - 0.00388 \\ - 0.00132 \\ + 0.00019 \\ \end{array}$	$\begin{array}{c} +0\cdot25414\\ -1\cdot11864\\ -0\cdot61235\\ -0\cdot03761\\ -1\cdot35488\\ +0\cdot61760\\ -1\cdot39765\\ +0\cdot11718\\ -2\cdot45014\\ +0\cdot44623\\ +0\cdot68905\\ -0\cdot13970\\ -0\cdot04122\\ +0\cdot00902\\ +0\cdot00071\\ -0\cdot00021\\ \end{array}$	$\begin{array}{c} 0\cdot00000\\ -1\cdot22990\\ 0\cdot00000\\ -0\cdot05305\\ 0\cdot00000\\ +1\cdot46080\\ 0\cdot00000\\ +1\cdot37465\\ 0\cdot00000\\ -1\cdot69780\\ 0\cdot00000\\ -1\cdot69780\\ 0\cdot00000\\ -1\cdot69780\\ 0\cdot00000\\ -1\cdot69780\\ 0\cdot00000\\ +0\cdot24110\\ 0\cdot00000\\ -0\cdot01091\\ 0\cdot00000\\ +0\cdot00022\\ \end{array}$
$egin{array}{c} C_1 \\ C_2 \end{array}$		-1.74729 + 3.90109	$+5.85920 \\ -2.79478$	+ 2 · 31547 + 1 · 83626	+0.73785 +3.39176	+2.59641 $-3.19970$	$-2 \cdot 92693 \\ -1 \cdot 74586$	$-4 \cdot 91234 \\ -0 \cdot 10613$	0·00000 +0·08511

Table VI.

$$(-1)^n (2n+1) \cdot \frac{S_n^2}{|E_n|^2} \cdot P_n$$
.  $\kappa a = 10$ .

n.	0°.	10°.	20°.	30°.	45°.	60°.	70°.	80°.	90°.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16		- 1·80103 + 2·81320 - 0·93383 + 7·67733 - 2·23712 + 1·39730 - 8·10718 + 8·01235 - 3·55304 + 0·83075 - 0·10061 + 0·00552 - 0·00007 - 0·00001	$\begin{array}{c} -1.71854 \\ +2.42946 \\ -0.68188 \\ +4.27386 \\ -0.77471 \\ +0.14262 \\ +1.41020 \\ -3.86670 \\ +2.95556 \\ -1.03705 \\ +0.18302 \\ -0.01615 \\ +0.00071 \\ -0.00001 \end{array}$	$\begin{array}{c} -1.58380 \\ +1.84154 \\ -0.33306 \\ +0.21089 \\ +0.63710 \\ -0.74187 \\ +5.39448 \\ -5.20152 \\ +1.59313 \\ -0.01819 \\ -0.07350 \\ +0.01251 \\ -0.00081 \\ +0.00002 \end{array}$	$\begin{array}{c} -1 \cdot 29318 \\ +0 \cdot 73662 \\ +0 \cdot 18130 \\ -3 \cdot 65545 \\ +1 \cdot 07192 \\ -0 \cdot 29442 \\ -1 \cdot 67101 \\ +4 \cdot 58070 \\ -2 \cdot 39955 \\ +0 \cdot 29750 \\ +0 \cdot 04765 \\ -0 \cdot 01129 \\ +0 \cdot 00063 \\ -0 \cdot 00001 \\ \end{array}$	$\begin{array}{c} -0.91441 \\ -0.36831 \\ +0.44868 \\ -2.60100 \\ -0.25637 \\ +0.64115 \\ -2.93474 \\ -1.13066 \\ +2.25133 \\ -0.48648 \\ -0.02921 \\ +0.01070 \\ -0.00044 \\ -0.00001 \end{array}$	$\begin{array}{c} -0.62549 \\ -0.95622 \\ +0.42356 \\ -0.03419 \\ -0.93614 \\ +0.41430 \\ +1.95346 \\ -4.26866 \\ +0.39989 \\ +0.56675 \\ -0.08527 \\ -0.00361 \\ +0.00059 \\ -0.00001 \\ \end{array}$	$\begin{array}{c} -0.31757 \\ -1.33995 \\ +0.25371 \\ +2.39260 \\ -0.80188 \\ -0.26206 \\ +3.72821 \\ +0.35787 \\ -2.18183 \\ +0.16717 \\ +0.09815 \\ -0.00598 \\ -0.00041 \\ +0.00002 \end{array}$	$\begin{array}{c} 0\cdot00000\\ -1\cdot47323\\ 0\cdot00000\\ +3\cdot37430\\ 0\cdot00000\\ -0\cdot61984\\ 0\cdot00000\\ +4\cdot19840\\ 0\cdot00000\\ -0\cdot63602\\ 0\cdot00000\\ +0\cdot01033\\ 0\cdot00000\\ -0\cdot00000\\ -0\cdot00000\\ -0\cdot00000\\ \end{array}$
$egin{array}{c} \mathrm{D_1} \ \mathrm{D_2} \end{array}$		-16.73288 +20.73644	+1·37436 +1·92603	+5.63354 -3.89662	-4.06224 + 1.65365	$-1.43516 \\ -3.93461$	+1·13060 -4·28164	+0.77838 +1.30967	0.00000 + 4.85392

Note.—The gaps in Tables V. to VIII. corresponding to  $\theta = 0$  are left owing to the fact that the entries would be just double the corresponding entries in Tables I. to IV. respectively, as is shown at the end of § 2.

Table VII.

$$(-1)^n \cdot (2n+1) \cdot \frac{S'_n C'_n}{|E'_n|^2} \cdot P_n$$
  $\kappa a = 10$ .

n.	0°.	10°.	20°.	30°.	45°.	60°.	70°.	80°.	90°.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17		$\begin{array}{c} -1 \cdot 44192 \\ -2 \cdot 34579 \\ -2 \cdot 22234 \\ +0 \cdot 22206 \\ +3 \cdot 87374 \\ +3 \cdot 01592 \\ -3 \cdot 53118 \\ -1 \cdot 47717 \\ +3 \cdot 51868 \\ -2 \cdot 95679 \\ +1 \cdot 18662 \\ -0 \cdot 19247 \\ +0 \cdot 00884 \\ +0 \cdot 00404 \\ -0 \cdot 00139 \\ +0 \cdot 00027 \\ -0 \cdot 00004 \end{array}$	$\begin{array}{c} -1 \cdot 37588 \\ -2 \cdot 02582 \\ -1 \cdot 62274 \\ +0 \cdot 12362 \\ +1 \cdot 34147 \\ +0 \cdot 30783 \\ +0 \cdot 61423 \\ +0 \cdot 71287 \\ -2 \cdot 92698 \\ +3 \cdot 69114 \\ -2 \cdot 15849 \\ +0 \cdot 56331 \\ -0 \cdot 09382 \\ +0 \cdot 01002 \\ -0 \cdot 00036 \\ -0 \cdot 00010 \\ +0 \cdot 00002 \end{array}$	$\begin{array}{c} -1 \cdot 26800 \\ -1 \cdot 53557 \\ -0 \cdot 79261 \\ +0 \cdot 00610 \\ -1 \cdot 10319 \\ -1 \cdot 60125 \\ +2 \cdot 34963 \\ +0 \cdot 95896 \\ -1 \cdot 57772 \\ +0 \cdot 06474 \\ +0 \cdot 86690 \\ -0 \cdot 43616 \\ +0 \cdot 10725 \\ -0 \cdot 01633 \\ +0 \cdot 00141 \\ -0 \cdot 00000 \\ -0 \cdot 00002 \end{array}$	$\begin{array}{c} -1 \cdot 03533 \\ -0 \cdot 61423 \\ +0 \cdot 43145 \\ -0 \cdot 10573 \\ -1 \cdot 85609 \\ -0 \cdot 63548 \\ -0 \cdot 72783 \\ -0 \cdot 84450 \\ +2 \cdot 37635 \\ -1 \cdot 05886 \\ -0 \cdot 56200 \\ +0 \cdot 39388 \\ -0 \cdot 08670 \\ +0 \cdot 000615 \\ +0 \cdot 00087 \\ -0 \cdot 00027 \\ +0 \cdot 00003 \end{array}$	$\begin{array}{c} -0.73208 \\ +0.30711 \\ +1.06778 \\ -0.07523 \\ +0.44393 \\ +1.38385 \\ -1.27826 \\ +0.20845 \\ -2.22956 \\ +1.73145 \\ +0.34455 \\ -0.37318 \\ +0.05799 \\ +0.00361 \\ -0.00201 \\ +0.000019 \\ +0.00001 \\ \end{array}$	$\begin{array}{c} -0.50077 \\ +0.79735 \\ +1.00800 \\ -0.00099 \\ +1.62098 \\ +0.89423 \\ +0.85080 \\ +0.78697 \\ -0.39602 \\ -2.01716 \\ +1.00575 \\ +0.12579 \\ -0.07831 \\ +0.00471 \\ +0.00153 \\ -0.00022 \\ -0.00000 \end{array}$	$\begin{array}{c} -0\cdot25425 \\ +1\cdot11733 \\ +0\cdot60377 \\ +0\cdot06921 \\ +1\cdot38851 \\ -0\cdot56563 \\ +1\cdot62387 \\ -0\cdot06598 \\ +2\cdot16073 \\ -0\cdot59498 \\ -1\cdot15752 \\ +0\cdot20867 \\ +0\cdot05401 \\ -0\cdot01094 \\ -0\cdot00082 \\ +0\cdot00024 \\ -0\cdot00000 \end{array}$	$\begin{array}{c} 0\cdot00000\\ +1\cdot22848\\ 0\cdot00000\\ +0\cdot09760\\ 0\cdot00000\\ -1\cdot33786\\ 0\cdot00000\\ -0\cdot77403\\ 0\cdot00000\\ +2\cdot26371\\ 0\cdot00000\\ -0\cdot36014\\ 0\cdot00000\\ +0\cdot01323\\ 0\cdot00000\\ -0\cdot00024\\ 0\cdot00000\\ \end{array}$
C' <sub>1</sub> C' <sub>2</sub>		$+1.39101 \\ -3.72993$	$ \begin{array}{r} -6 \cdot 22255 \\ +3 \cdot 38287 \end{array} $	$-1 \cdot 41635 \\ -2 \cdot 55951$	$-1.45925 \\ -2.85904$	$ \begin{array}{r} -2 \cdot 32765 \\ +3 \cdot 18625 \end{array} $	+3.51196 +0.59068	+ 4 · 41830 + 0 · 15792	0.000000 + 1.13075

TABLE VIII.

$$(-1)^n \cdot (2n+1) \cdot \frac{(S'_n)^2}{|E'_n|^2} \cdot P_n$$
.  $\kappa a = 10$ .

n.	О°.	10°.	20°.	30°.	45°.	60°.	70°.	80°.	90°.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16		$\begin{array}{c} -1.15625 \\ +1.94572 \\ -5.47142 \\ +0.00643 \\ -6.20597 \\ +8.02454 \\ -1.63904 \\ +0.25319 \\ -2.07970 \\ +1.74759 \\ -0.29624 \\ +0.01234 \\ -0.00011 \\ -0.00001 \end{array}$	$\begin{array}{c} -1 \cdot 10329 \\ +1 \cdot 68031 \\ -3 \cdot 99521 \\ +0 \cdot 00358 \\ -2 \cdot 14912 \\ +0 \cdot 81905 \\ +0 \cdot 28510 \\ -0 \cdot 12219 \\ +1 \cdot 72998 \\ -2 \cdot 18162 \\ +0 \cdot 53763 \\ -0 \cdot 03612 \\ +0 \cdot 00122 \\ -0 \cdot 00002 \\ \end{array}$	$\begin{array}{c} -1\cdot01679 \\ +1\cdot27368 \\ -1\cdot95142 \\ +0\cdot00018 \\ +1\cdot76738 \\ -4\cdot26049 \\ +1\cdot09061 \\ -0\cdot16437 \\ +0\cdot93250 \\ -0\cdot21592 \\ +0\cdot02797 \\ -0\cdot00139 \\ +0\cdot00004 \\ \end{array}$	$\begin{array}{c} -0.83021 \\ +0.50947 \\ +1.06223 \\ -0.00306 \\ +2.97358 \\ -1.69083 \\ -0.33783 \\ +0.14475 \\ -1.40453 \\ +0.13998 \\ -0.02526 \\ +0.00108 \\ -0.00001 \\ \end{array}$	$\begin{array}{c} -0.58704 \\ -0.25474 \\ +2.62888 \\ -0.00218 \\ -0.71120 \\ +3.68205 \\ -0.59332 \\ -0.03573 \\ +1.31777 \\ -1.02336 \\ -0.08582 \\ +0.02393 \\ -0.00075 \\ +0.00001 \end{array}$	$\begin{array}{c} -0\cdot 40156 \\ -0\cdot 66136 \\ +2\cdot 48170 \\ -0\cdot 00003 \\ -2\cdot 59693 \\ +2\cdot 37930 \\ +0\cdot 39491 \\ -0\cdot 13489 \\ +0\cdot 23407 \\ +1\cdot 19223 \\ -0\cdot 25051 \\ -0\cdot 00807 \\ +0\cdot 00101 \\ -0\cdot 00001 \end{array}$	$\begin{array}{c} -0\cdot20388\\ -0\cdot92677\\ +1\cdot48648\\ +0\cdot00200\\ -2\cdot22449\\ -1\cdot50498\\ +0\cdot75374\\ +0\cdot01131\\ -1\cdot27709\\ +0\cdot35166\\ +0\cdot28831\\ -0\cdot01338\\ -0\cdot00070\\ +0\cdot00002\\ \end{array}$	$\begin{array}{c} 0\cdot00000\\ -1\cdot01895\\ 0\cdot00000\\ +0\cdot00282\\ 0\cdot00000\\ -3\cdot55967\\ 0\cdot00000\\ +0\cdot13267\\ 0\cdot00000\\ -1\cdot33795\\ 0\cdot00000\\ +0\cdot02309\\ 0\cdot00000\\ -0\cdot00003\\ \end{array}$
$\begin{array}{c} D'_1 \\ D'_2 \end{array}$		$ \begin{array}{r} -16.84873 \\ +11.98980 \end{array} $	$\begin{vmatrix} -4.69369 \\ +0.16299 \end{vmatrix}$	+0:60497 -3:16125	+1:60430 -0:43910	+ 1 · 96852 + 2 · 38996	$ \begin{array}{r} -0.13731 \\ +2.76717 \end{array} $	$ \begin{vmatrix} -1 \cdot 17763 \\ -2 \cdot 08014 \end{vmatrix} $	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$

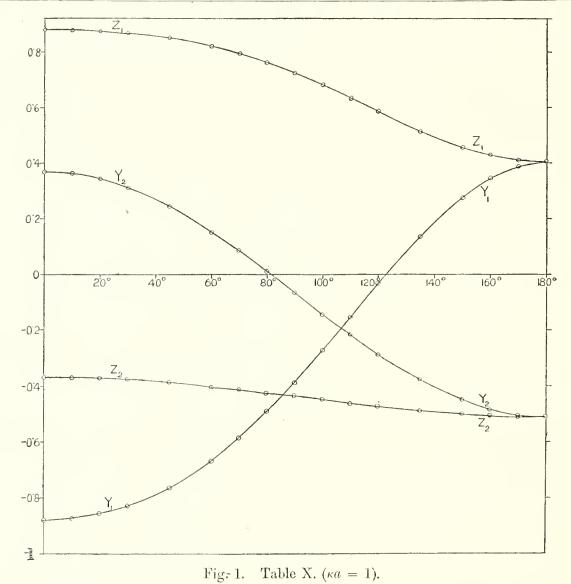
Note.—The gaps in Tables V. to VIII. corresponding to  $\theta = 0$  are left owing to the fact that the entries would be just double the corresponding entries in Tables I. to IV. respectively, as is shown at the end of § 2.

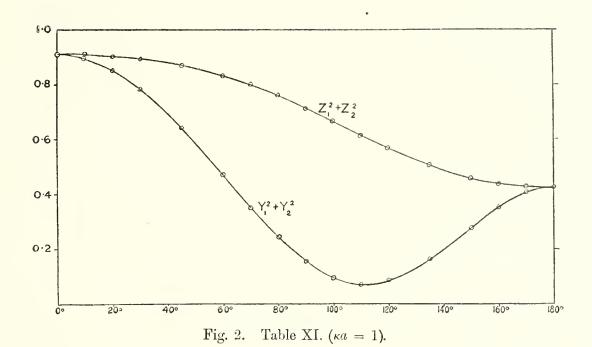
TABLE X.

		$\kappa a$	= 1.			ка	= 2.			
θ.	Y <sub>1</sub> .	$Y_2$ .	$Z_1$ .	$Z_2$ .	Y <sub>1</sub> .	$Y_2$ .	$Z_1$ .	$Z_2$ .		
0	-0.87964	+0.36828	+0.87964	-0.36828	-0.01686	-1.00392	+0.01686	+1.00392		
10	-0.87409	+0.36177	+0.87833	-0.36931	-0.05133	-0.97319	+0.03713	+0.98979		
20	-0.85739	+0.34240	+0.87421	-0.37235	-0.15388	-0.88511	+0.09780	+0.94713		
30	-0.82898	+0.31068	+0.86695	-0.37735	-0.32775	-0.75189	+0.19180	+0.87470		
45	-0.76305	+0.24213	+0.84886	-0.38814	-0.67558	-0.50959	+0.41394	+0.70713		
60	-0.66730	+0.15213	+0.82006	-0.40234	-1.10637	-0.28864	+0.68944	+0.46459		
70	-0.58650	+0.08407	+0.79396	-0.41326	-1.39254	-0.19417	+0.88593	+0.26063		
80	-0.49274	+0.01031	+0.76198	-0.42497	-1.63685	-0.16609	+1.07223	+0.02454		
90	-0.38750	-0.06572	+0.72430	-0.43714	-1.80040	-0.21751	+1:22758	-0.23984		
100	-0.27326	-0.14203	+0.68166	-0.44941	-1.84751	-0.35271	+1.33131	-0.52610		
110	-0.15360	-0.21597	+0.63534	-0.46136	-1.75394	-0.56577	+1.36711	-0.82519		
120	-0.03310	-0.28649	+0.58728	-0.47266	-1.51443	-0.84086	+1.32726	-1.12573		
135	+0.13733	-0.37819	+0.51714	-0.48762	-0.93146	-1:31449	+1:14028	-1:54979		
150	+0.27800	-0.44904	+0.45767	-0.49917	-0.23151	-1.76695	+0.86400	-1.89896		
160	+0.34623	-0.48198	+0.42835	-0.50453	+0.16600	-2.00347	+0.70070	-2.06803		
170	+0.38897	-0.50215	+0.40985	-0.50783	+0.44169	-2.15677	+0.58211	-2.17383		
180	+0.40352	-0.50896	+0.40352	-0.50896	+0.53950	-2.20986	+0.53950	-2.20986		
							<u> </u>			
		κα :	= 9.		$\kappa a = 10.$					
$\theta$ .	Y <sub>1</sub> .	$\mathbf{Y}_{2}$ .	$Z_1$ .	$Z_2$ .	$Y_1$ .	$Y_2$ .	$Z_1$ .	$Z_2$ .		
•	. 0 00110	2 02040	0.00110	0.0000	2.0100	1 07 05	0.0100	4 OF AF		
0	+2.92118	- 2.92969	-2.92118	+ 2.92969	+2.0189	+ 4.3765	-2.0189	- 4.3765		
10	+2.85178	- 3.44035		+ 3.25040	+2.2090	+ 4.5747	-2.3163	-4.3554 $-3.9348$		
$\frac{20}{30}$	+2.39601 +0.93972	$\begin{vmatrix} - & 4 \cdot 21198 \\ - & 4 \cdot 34162 \end{vmatrix}$	$\begin{vmatrix} -2 \cdot 11542 \\ -0 \cdot 77288 \end{vmatrix}$	+ 3.96256	+2.8996	$\begin{vmatrix} + & 4.1626 \\ + & 2.3038 \end{vmatrix}$	-3.1586 $-4.3085$	$\begin{bmatrix} -3.9348 \\ -2.5090 \end{bmatrix}$		
30	+0.93912	- 4 34162	-0.11288	+ 4.50196	+4.2579	+ 2.9090	-4.2009	- 2.3090		
45										
	-2.79263	- 3.71421	+2.55340	+ 3.69379	+4.9757	- 1.3455	-4.7881	+ 1:6373		
60	$\begin{vmatrix} -2.79263 \\ -4.11873 \end{vmatrix}$									
60 70	-4.11873	- 0.09190	+4.54564	- 0.28764	+0.1954	- 5.0860	-0.3981	+ 4.9827		
60 70 80										
70	$\begin{bmatrix} -4 \cdot 11873 \\ -2 \cdot 65205 \end{bmatrix}$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{vmatrix} +4.54564 \\ +2.71046 \end{vmatrix}$	$\begin{vmatrix} - & 0.28764 \\ - & 3.61300 \end{vmatrix}$	$+0.1954 \\ -3.2701$	- 5·0860 - 3·8259	-0.3981 + 3.8519	+ 4·9827 + 3·3399		
70 80 90	$ \begin{array}{r} -4 \cdot 11873 \\ -2 \cdot 65205 \\ +0 \cdot 44242 \\ +4 \cdot 07803 \end{array} $	- 0.09190 + 3.87786 + 4.55372 + 0.45069	$ \begin{vmatrix} +4.54564 \\ +2.71046 \\ -1.41433 \end{vmatrix} $ $ -4.49231 $	- 0.28764 - 3.61300 + 4.42270 - 0.87232	$   \begin{array}{r}     +0.1954 \\     -3.2701 \\     -4.4103 \\     -1.3987   \end{array} $	- 5.0860 - 3.8259 + 1.9553 + 5.0868	$ \begin{array}{r} -0.3981 \\ +3.8519 \\ +4.7201 \\ +0.1429 \end{array} $	+ 4.9827 + 3.3399 - 1.7529 - 5.1878		
70 80 90 100	$ \begin{array}{r} -4 \cdot 11873 \\ -2 \cdot 65205 \\ +0 \cdot 44242 \\ +4 \cdot 07803 \\ +3 \cdot 98050 \end{array} $	- 0.09190 + 3.87786 + 4.55372 + 0.45069 - 3.34098	$\begin{vmatrix} +4.54564 \\ +2.71046 \\ -1.41433 \end{vmatrix}$ $-4.49231$ $-2.63233$	$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$   \begin{vmatrix}     +0.1954 \\     -3.2701 \\     -4.4103   \end{vmatrix}   $ $   -1.3987 \\    +4.5127 $	- 5.0860 - 3.8259 + 1.9553 + 5.0868 + 0.9681	$ \begin{array}{r} -0.3981 \\ +3.8519 \\ +4.7201 \\ +0.1429 \\ -4.9162 \end{array} $	+ 4.9827 + 3.3399 - 1.7529 - 5.1878 - 1.5245		
70 80 90	$ \begin{array}{r} -4 \cdot 11873 \\ -2 \cdot 65205 \\ +0 \cdot 44242 \\ +4 \cdot 07803 \end{array} $	- 0.09190 + 3.87786 + 4.55372 + 0.45069	$ \begin{vmatrix} +4.54564 \\ +2.71046 \\ -1.41433 \end{vmatrix} $ $ -4.49231 $	- 0.28764 - 3.61300 + 4.42270 - 0.87232	$   \begin{array}{r}     +0.1954 \\     -3.2701 \\     -4.4103 \\     -1.3987 \\     +4.5127 \\     +4.2248   \end{array} $	- 5.0860 - 3.8259 + 1.9553 + 5.0868	$ \begin{array}{r} -0.3981 \\ +3.8519 \\ +4.7201 \\ +0.1429 \end{array} $	+ 4.9827 + 3.3399 - 1.7529 - 5.1878		
70 80 90 100 110	$ \begin{array}{r} -4 \cdot 11873 \\ -2 \cdot 65205 \\ +0 \cdot 44242 \\ +4 \cdot 07803 \\ +3 \cdot 98050 \\ -2 \cdot 08115 \end{array} $	- 0.09190 + 3.87786 + 4.55372 + 0.45069 - 3.34098 - 2.44198	$\begin{vmatrix} +4.54564 \\ +2.71046 \\ -1.41433 \end{vmatrix}$ $-4.49231$ $-2.63233 \\ +2.93266$	$ \begin{array}{r} -0.28764 \\ -3.61300 \\ +4.42270 \end{array} $ $ -0.87232 \\ +3.98232 \\ +3.77514 $	$   \begin{vmatrix}     +0.1954 \\     -3.2701 \\     -4.4103   \end{vmatrix}   $ $   -1.3987 \\    +4.5127 $	$ \begin{array}{r} -5.0860 \\ -3.8259 \\ +1.9553 \end{array} $ $ +5.0868 \\ +0.9681 \\ -3.2744 $	$ \begin{array}{r} -0.3981 \\ +3.8519 \\ +4.7201 \\ +0.1429 \\ -4.9162 \\ -2.4495 \end{array} $	+ 4.9827 + 3.3399 - 1.7529 - 5.1878 - 1.5245 + 4.8109		
70 80 90 100 110 120	$ \begin{array}{r} -4 \cdot 11873 \\ -2 \cdot 65205 \\ +0 \cdot 44242 \\ +4 \cdot 07803 \\ +3 \cdot 98050 \\ -2 \cdot 08115 \\ -5 \cdot 97919 \\ +4 \cdot 89401 \end{array} $	$ \begin{array}{r} - 0.09190 \\ + 3.87786 \\ + 4.55372 \\ + 0.45069 \\ - 3.34098 \\ - 2.44198 \\ + 0.37778 \\ + 2.22161 \end{array} $	$\begin{vmatrix} +4.54564 \\ +2.71046 \\ -1.41433 \end{vmatrix}$ $-4.49231$ $-2.63233 \\ +2.93266 \\ +4.53082$ $-4.61842$	$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$   \begin{array}{r}     +0.1954 \\     -3.2701 \\     -4.4103   \end{array} $ $     -1.3987 \\     +4.5127 \\     +4.2248 \\     -4.4893 \\     +0.3279   \end{array} $	$ \begin{array}{r} -5.0860 \\ -3.8259 \\ +1.9553 \end{array} $ $ +5.0868 \\ +0.9681 \\ -3.2744 \\ -1.9474 \\ +1.5395 $	$ \begin{array}{r} -0.3981 \\ +3.8519 \\ +4.7201 \\ +0.1429 \\ -4.9162 \\ -2.4495 \\ +4.6565 \\ -1.5266 \end{array} $	+ 4.9827 + 3.3399 - 1.7529 - 5.1878 - 1.5245 + 4.8109 + 2.8540 - 6.0371		
70 80 90 100 110 120 135	$ \begin{array}{r} -4 \cdot 11873 \\ -2 \cdot 65205 \\ +0 \cdot 44242 \\ +4 \cdot 07803 \\ +3 \cdot 98050 \\ -2 \cdot 08115 \\ -5 \cdot 97919 \\ +4 \cdot 89401 \\ +0 \cdot 17682 \end{array} $	$ \begin{array}{r} - \ 0 \cdot 09190 \\ + \ 3 \cdot 87786 \\ + \ 4 \cdot 55372 \\ + \ 0 \cdot 45069 \\ - \ 3 \cdot 34098 \\ - \ 2 \cdot 44198 \\ + \ 0 \cdot 37778 \\ + \ 2 \cdot 22161 \\ + \ 1 \cdot 81954 \end{array} $	$\begin{vmatrix} +4.54564 \\ +2.71046 \\ -1.41433 \end{vmatrix}$ $-4.49231$ $-2.63233 \\ +2.93266 \\ +4.53082$ $-4.61842$ $+0.68260$	$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$   \begin{array}{r}     +0.1954 \\     -3.2701 \\     -4.4103   \end{array} $ $     -1.3987 \\     +4.5127 \\     +4.2248 \\     -4.4893 \\     +0.3279 \\     +4.2427   \end{array} $	- 5.0860 - 3.8259 + 1.9553 + 5.0868 + 0.9681 - 3.2744 - 1.9474 + 1.5395 + 4.1158	$ \begin{array}{r} -0.3981 \\ +3.8519 \\ +4.7201 \end{array} $ $ +0.1429 \\ -4.9162 \\ -2.4495 \\ +4.6565 \\ -1.5266 \\ -2.6272 $	+ 4.9827 + 3.3399 - 1.7529 - 5.1878 - 1.5245 + 4.8109 + 2.8540 - 6.0371 + 8.0995		
70 80 90 100 110 120 135 150 160	$ \begin{array}{r} -4 \cdot 11873 \\ -2 \cdot 65205 \\ +0 \cdot 44242 \\ +4 \cdot 07803 \\ +3 \cdot 98050 \\ -2 \cdot 08115 \\ -5 \cdot 97919 \\ +4 \cdot 89401 \\ +0 \cdot 17682 \\ -9 \cdot 31245 \end{array} $	$\begin{array}{c} -0.09190 \\ +3.87786 \\ +4.55372 \\ +0.45069 \\ -3.34098 \\ -2.44198 \\ +0.37778 \\ +2.22161 \\ +1.81954 \\ -10.01990 \\ \end{array}$	$\begin{array}{c} + 4.54564 \\ + 2.71046 \\ - 1.41433 \\ - 4.49231 \\ - 2.63233 \\ + 2.93266 \\ + 4.53082 \\ - 4.61842 \\ + 0.68260 \\ + 8.06560 \end{array}$	$\begin{array}{c} -0.28764 \\ -3.61300 \\ +4.42270 \\ -0.87232 \\ +3.98232 \\ +3.77514 \\ -2.25240 \\ -2.86833 \\ +7.60056 \\ -3.40086 \end{array}$	$   \begin{array}{r}     +0.1954 \\     -3.2701 \\     -4.4103   \end{array} $ $     -1.3987 \\     +4.5127 \\     +4.2248 \\     -4.4893 \\     +0.3279 \\     +4.2427 \\     -9.2435   \end{array} $	$ \begin{array}{r} -5.0860 \\ -3.8259 \\ +1.9553 \end{array} $ $ +5.0868 \\ +0.9681 \\ -3.2744 \\ -1.9474 \\ +1.5395 \\ +4.1158 \\ -7.4971 $	$ \begin{array}{r} -0.3981 \\ +3.8519 \\ +4.7201 \end{array} $ $ +0.1429 \\ -4.9162 \\ -2.4495 \\ +4.6565 \\ -1.5266 \\ -2.6272 \\ +8.2673 $	+ 4.9827 + 3.3399 - 1.7529 - 5.1878 - 1.5245 + 4.8109 + 2.8540 - 6.0371 + 8.0995 + 0.7136		
70 80 90 100 110 120 135	$ \begin{array}{r} -4 \cdot 11873 \\ -2 \cdot 65205 \\ +0 \cdot 44242 \\ +4 \cdot 07803 \\ +3 \cdot 98050 \\ -2 \cdot 08115 \\ -5 \cdot 97919 \\ +4 \cdot 89401 \\ +0 \cdot 17682 \end{array} $	$ \begin{array}{r} - \ 0 \cdot 09190 \\ + \ 3 \cdot 87786 \\ + \ 4 \cdot 55372 \\ + \ 0 \cdot 45069 \\ - \ 3 \cdot 34098 \\ - \ 2 \cdot 44198 \\ + \ 0 \cdot 37778 \\ + \ 2 \cdot 22161 \\ + \ 1 \cdot 81954 \end{array} $	$\begin{vmatrix} +4.54564 \\ +2.71046 \\ -1.41433 \end{vmatrix}$ $-4.49231$ $-2.63233 \\ +2.93266 \\ +4.53082$ $-4.61842$ $+0.68260$	$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$   \begin{array}{r}     +0.1954 \\     -3.2701 \\     -4.4103   \end{array} $ $     -1.3987 \\     +4.5127 \\     +4.2248 \\     -4.4893 \\     +0.3279 \\     +4.2427   \end{array} $	- 5.0860 - 3.8259 + 1.9553 + 5.0868 + 0.9681 - 3.2744 - 1.9474 + 1.5395 + 4.1158	$ \begin{array}{r} -0.3981 \\ +3.8519 \\ +4.7201 \end{array} $ $ +0.1429 \\ -4.9162 \\ -2.4495 \\ +4.6565 \\ -1.5266 \\ -2.6272 $	+ 4.9827 + 3.3399 - 1.7529 - 5.1878 - 1.5245 + 4.8109 + 2.8540 - 6.0371 + 8.0995		

Table XI.

$\theta$ .	κα =	= 1.	ка =	= 2.	ка =	= 9.	κa =	= 10.
0.	$Y_1^2 + Y_2^2$ .	$Z_1^2 + Z_2^2$ .	$Y_1^2 + Y_2^2$ .	$Z_1^2 + Z_2^2$ .	$Y_1^2 + Y_2^2$ .	$Z_1^2 + Z_2^2$ .	$Y_1^2 + Y_2^2$ .	$Z_1^2 + Z_2^2$ .
0 10 20 30	0.9094 $0.8949$ $0.8524$ $0.7837$	0.9094 $0.9079$ $0.9029$ $0.8940$	1·0081 0·9497 0·8071 0·6728	1·0081 0·9811 0·9066 0·8019	$ \begin{array}{ c c c c } \hline 17.12 \\ 19.97 \\ 23.48 \\ 19.73 \end{array} $	$   \begin{array}{r}     17 \cdot 12 \\     18 \cdot 11 \\     20 \cdot 18 \\     20 \cdot 86   \end{array} $	$23 \cdot 23$ $25 \cdot 81$ $25 \cdot 74$ $23 \cdot 44$	$23 \cdot 23$ $24 \cdot 33$ $25 \cdot 46$ $24 \cdot 86$
45	0.6409	0.8712	0.7161	0.6714	21.59	20.16	26.57	25.61
60 70 80	$0.4684 \\ 0.3511 \\ 0.2429$	$0.8344 \\ 0.8012 \\ 0.7612$	$1 \cdot 3074 \\ 1 \cdot 9769 \\ 2 \cdot 7069$	0.6912 $0.8528$ $1.1503$	$ \begin{array}{c c} 16 \cdot 97 \\ 22 \cdot 07 \\ 20 \cdot 93 \end{array} $	$20.75 \\ 20.40 \\ 21.56$	$\begin{array}{c} 25 \cdot 91 \\ 25 \cdot 33 \\ 23 \cdot 27 \end{array}$	$24 \cdot 99$ $25 \cdot 99$ $25 \cdot 35$
90	0.1545	0.7157	3 · 2887	1.5645	16.83	20.94	27.83	26.93
$ \begin{array}{ c c c c } 100 \\ 110 \\ 120 \\ \end{array} $	0.0948 $0.0702$ $0.0832$	$0.6666 \\ 0.6165 \\ 0.5683$	3.5377 $3.3964$ $3.0005$	$2 \cdot 0492$ $2 \cdot 5499$ $3 \cdot 0289$	$\begin{array}{c} 27 \cdot 01 \\ 10 \cdot 29 \\ 35 \cdot 89 \end{array}$	$22 \cdot 79$ $22 \cdot 85$ $25 \cdot 60$	$21 \cdot 30$ $28 \cdot 57$ $23 \cdot 95$	$ \begin{array}{c c} 26 \cdot 49 \\ 29 \cdot 14 \\ 29 \cdot 83 \end{array} $
135	0.1619	0.5052	$2 \cdot 5955$	$3 \cdot 7021$	28.89	29.56	2.48	38.78
150 160 170 180	0.2789 $0.3522$ $0.4035$ $0.4219$	0.4586 $0.4380$ $0.4259$ $0.4219$	$3 \cdot 1757$ $4 \cdot 0415$ $4 \cdot 8467$ $5 \cdot 1745$	$4 \cdot 3525$ $4 \cdot 7677$ $5 \cdot 0644$ $5 \cdot 1745$	$3 \cdot 34$ $187 \cdot 1$ $979 \cdot 7$ $1755$	$58 \cdot 23$ $76 \cdot 62$ $831 \cdot 0$ $1755$	$ \begin{array}{r} 34 \cdot 94 \\ 141 \cdot 65 \\ 1295 \\ 2659 \end{array} $	72·50 68·87 1046 2659





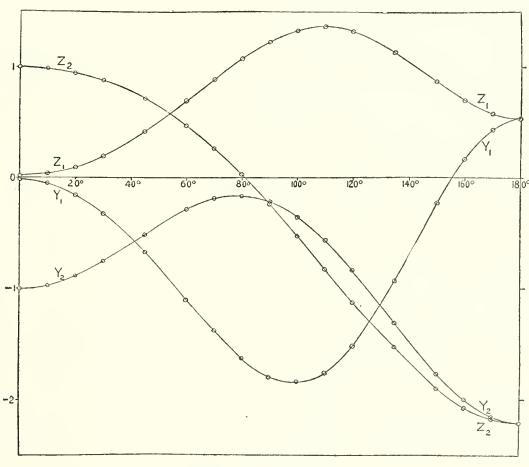
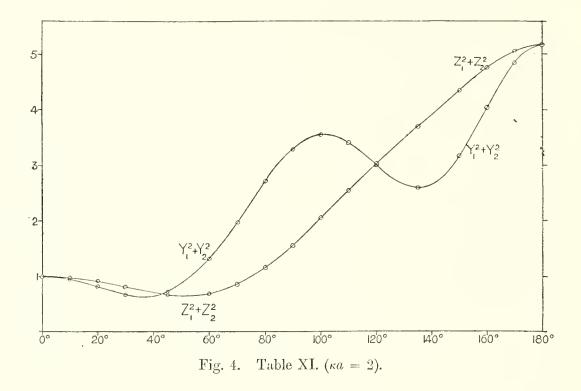


Fig. 3. Table X. ( $\kappa a = 2$ ).





Analysis of Results and Interpolation.

4. A consideration of the results tabulated up to this point shows that for  $\kappa a = 9$ , 10, they are not adequate for the complete representation of  $Y_1^2 + Y_2^2$ ,  $Z_1^2 + Z_2^2$  throughout the range of  $\theta$ . Owing to the excessive labour involved in further computations from the original series, other methods were tried. The following sections are devoted to the discussion and presentation of this work.

For values of  $\theta$ , except those "near" 180°, the first approximation for large values of  $\kappa a$ , gives

 $Y_{1} = -Z_{1} = \frac{1}{2}\kappa a \cos \theta,$   $Y_{2} = -Z_{2} = \frac{1}{2}\kappa a \sin \theta,$   $\Theta = 2\kappa a \cos \frac{1}{2} \theta.$ \*(10)

where

Consider then the functions

$$\eta_1 = Y_1 - \frac{1}{2}\kappa a \cos \Theta, \qquad \zeta_1 = Z_1 + \frac{1}{2}\kappa a \cos \Theta, 
\eta_2 = Y_2 - \frac{1}{2}\kappa a \sin \Theta, \qquad \zeta_2 = Z_2 + \frac{1}{2}\kappa a \sin \Theta,$$

$$\zeta_1 = Z_1 + \frac{1}{2}\kappa a \cos \Theta, 
\zeta_2 = Z_2 + \frac{1}{2}\kappa a \sin \Theta,$$
(11)

which express the amounts by which the functions  $Y_1$ ,  $Y_2$ ,  $Z_1$ ,  $Z_2$  differ from the values given by (10). These functions and their derivatives are calculable from the

preceding tables, at the values of  $\theta$  taken. Tables XX. to XXIII.\* give steps in the necessary computations, and figs. 5 to 12 show the results plotted against  $\theta$  from 0° to 150°. These curves show that for this range the first approximation is very good for  $Z_1$ ,  $Z_2$ . In fact, the curves for  $\xi_1$ ,  $\xi_2$  were easily drawn and gave interpolated values of  $Z_1$ ,  $Z_2$  to three places of decimals, the last figure being approximate. The functions  $\eta_1$ ,  $\eta_2$  have a greater number of oscillations and greater amplitudes, and there was in places some little doubt as to the exact forms of the curves. By careful examination and comparison of corresponding curves for the two cases of  $\kappa a = 9$  and 10, this difficulty was overcome. Such a comparison was more fruitful when the curves were plotted with  $\theta$  as abscissæ, and this was done with  $\eta_1$ ,  $\eta_2$ ,  $\xi_1$ ,  $\xi_2$ , though the curves are not given below. Corresponding curves are very similar but are not in phase with each other. In the range  $\theta = 0$ ° to 90°, it was found possible to obtain  $Y_1$ ,  $Y_2$  to at least two places of decimals, with very little doubt.

It was the work just described which led to the detection of errors mentioned in §§ 1, 3, How this was possible becomes evident on an examination of the formulæ and numbers. For example, an error in  $Y_1$  or  $Z_1$  generally leads to a larger relative error in  $\partial Y_1/\partial \theta$  and  $\partial Z_1/\partial \theta$ , to a much larger relative error in  $\eta_1$  or  $\xi_1$ , and to a very much larger relative error in  $\partial \eta_1/\partial \theta$  and  $\partial \eta_1/\partial \theta$ . Thus, an error might pass unsuspected in the graph of  $Y_1$  (for example) but render the drawing of the graph of  $\eta_1$  impossible. Irregularities could also be detected in the curves plotted with  $\theta$  as abscissæ. By these means it was possible easily to detect errors in  $Y_1$ ,  $Y_2$ ,  $Z_1$ ,  $Z_2$ , of the magnitude 0.01. The actual finding of the errors involved much patient revision of the summing of the series. Their existence had previously been entirely unsuspected.

In this part of the work it was necessary to calculate a number of values of  $\cos \Theta$  and  $\sin \Theta$ . The method adopted was to find  $\theta$  such that  $\Theta/\pi = r + \theta_1/180$ , where r is an integer and  $\theta_1 = 0^{\circ}$ ,  $10^{\circ}$ ,  $20^{\circ} \dots 170^{\circ}$ . This yielded about eighteen points on each undulation, and a selection from these was made according to circumstances.

\* Tables XXII., XXIII., and figs. 5 to 12 are not printed.

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Table XXII. gives \eta_1, \eta_2, &c. (\kappa a = 9, 10).

" XXIII. ,, \partial \eta_1/\partial \theta, \partial \eta_2/\partial \theta, &c. (\kappa a = 9, 10).

Fig. 5 gives the graph of \eta_1 (\kappa a = 9).

" 6 " " " \eta_1 (\kappa a = 10).

" 7 " " " \eta_2 (\kappa a = 9).

" 8 " " " \eta_2 (\kappa a = 9).

" 9 " " \zeta_1 (\kappa a = 10).

" 10 " " \zeta_2 (\kappa a = 9).

" 12 " " \zeta_2 (\kappa a = 9).
```

TABLE XX.

	$\kappa a = 9.$		$\theta$ .		$\kappa a = 10.$	
$180\Theta/\pi$ .	$\sin \Theta$ .	$\cos \Theta$ .	0.	$180\Theta/\pi$ .	$\sin \Theta$ .	$\cos \Theta$ .
$180\theta/\pi.$ $1031 \cdot 3240$ $1027 \cdot 3995$ $1015 \cdot 6558$ $996 \cdot 1825$ $952 \cdot 8189$ $893 \cdot 1527$ $844 \cdot 8112$ $790 \cdot 0400$ $729 \cdot 2561$ $662 \cdot 9223$ $591 \cdot 5431$ $515 \cdot 6620$	$ sin \Theta. $ $ -0.75099 $ $ -0.79442 $ $ -0.90141 $ $ -0.99418 $ $ -0.79673 $ $ +0.11922 $ $ +0.82104 $ $ +0.93993 $ $ +0.16085 $ $ -0.83941 $ $ -0.78308 $ $ +0.41212 $	$\cos \Theta$ .  + 0 · 66032 + 0 · 60737 + 0 · 43296 + 0 · 10770  - 0 · 60434  - 0 · 99287 - 0 · 57087 + 0 · 34136 + 0 · 98698  + 0 · 54350 - 0 · 62192 - 0 · 91113	0 10 20 30 45 60 70 80 90 100 110 120	$180\Theta/\pi$ . $1145 \cdot 9156$ $1141 \cdot 5550$ $1128 \cdot 5066$ $1106 \cdot 8694$ $1058 \cdot 6878$ $992 \cdot 3918$ $938 \cdot 6791$ $877 \cdot 8222$ $810 \cdot 2846$ $736 \cdot 5803$ $657 \cdot 2702$ $572 \cdot 9577$	$ sin \Theta. $ $ + 0.91295 + 0.87927 + 0.74903 + 0.45196 $ $ - 0.36345 - 0.99913 - 0.62496 + 0.37748 + 0.99999 + 0.28536 - 0.88886 - 0.54402$	$\begin{array}{c} \cos \theta. \\ \hline \\ +0.40808 \\ +0.47631 \\ +0.66253 \\ +0.89204 \\ \hline \\ +0.93161 \\ \hline \\ +0.04173 \\ -0.78066 \\ -0.92602 \\ \hline \\ -0.00497 \\ \hline \\ +0.95842 \\ +0.45819 \\ -0.83907 \\ \hline \end{array}$
$ \begin{array}{c} 394 \cdot 6706 \\ 266 \cdot 9263 \\ 179 \cdot 0876 \\ 89 \cdot 8858 \end{array} $	+0.56880 $-0.99856$ $+0.01592$ $+1.00000$	+0.82244 $-0.05362$ $-0.99987$	$   \begin{array}{c}     135 \\     150 \\     160 \\     170   \end{array} $	438·5229 296·5847 198·9861	+ 0.98000 - 0.89427 - 0.32534	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$
0.0000	0.00000	+0.00199	180	99.8731	+0.98519	+1.00000

### TABLE XXI.

$\kappa a$	= 9.		$\kappa a =$	= 10.
$\frac{\partial}{\partial \theta}$ . $\sin \Theta$ .	$\frac{\partial}{\partial \theta}$ . cos $\Theta$ .	$\theta$ .	$\frac{\partial}{\partial \theta}$ . $\sin \Theta$ .	$\frac{\partial}{\partial \theta} \cdot \cos \Theta$ .
		0		
0.00000	0.00000	0	0.00000	0.00000
-0.00832	-0.01088	10	-0.00725	+0.01337
-0.01181	-0.02459	20	-0.02008	+0.02270
-0.00438	-0.04042	30	-0.04029	+0.02042
+0.03633	-0.04789	45	-0.06222	-0.02428
+0.07798	+0.00936	60	-0.00364	-0.08719
+0.05143	+0.07397	70	+0.07815	-0.06256
-0.03447	+0.09491	80	+0.10389	+0.04235
-0.10963	+0.01787	90	+0.00061	+0.12341
-0.06540	-0.10100	100	-0.12814	+0.03815
+0.08002	-0.10076	110	-0.06551	-0.12708
+0.12395	+0.05606	120	+0.12683	-0.08223
-0.11936	+0.08255	135	-0.03208	+0.15802
+0.00814	-0.15151	150	-0.07544	-0.15076
+0.15467	+0.00246	160	+0.16253	-0.05592
-0.00031	+0.15648	170	+0.02977	+0.17129
-0.15708	+0.00000	180	+0.17453	+0.00000

5. There remains the discussion of  $Y_1$ ,  $Y_2$  for the range  $\theta = 90^{\circ}$  to 180°, and of  $Z_1$ ,  $Z_2$  for the range  $\theta = 120^{\circ}$  to 180°. For portions of these ranges a method was used which consists in decomposing  $\eta_1$ ,  $\eta_2$ ,  $\xi_1$ ,  $\xi_2$  into functions for which graphical interpolation is easier.

For both  $\kappa a = 9$  and 10, take

$$\eta_1 = \alpha_1 \cos \Theta + \beta_1 \sin \Theta, \qquad \xi_1 = \gamma_1 \cos \Theta + \delta_1 \sin \Theta, 
\eta_2 = \alpha_2 \cos \Theta + \beta_2 \sin \Theta, \qquad \xi_2 = \gamma_2 \cos \Theta + \delta_2 \sin \Theta,$$

$$(12)$$

where  $\alpha_1$ ,  $\alpha_2$ ,  $\beta_1$ ,  $\beta_2$ ,  $\gamma_1$ ,  $\gamma_2$ ,  $\delta_1$ ,  $\delta_2$  are functions of  $\theta$  only.

These functions, thus defined, are perfectly determinate, but they can only be used for  $\kappa a = 9$ , 10. Together with their derivatives, they are calculable for the tabulated values of  $\theta$ . We have, in fact,

$$\alpha_{1} = \frac{\Delta (\eta_{1}/\sin \Theta)}{\Delta (\cot \Theta)}, \qquad \beta_{1} = \frac{\Delta (\eta_{1}/\cos \Theta)}{\Delta (\tan \Theta)},$$

$$\alpha_{2} = \frac{\Delta (\eta_{2}/\cos \Theta)}{\Delta (\tan \Theta)}, \qquad \beta_{2} = \frac{\Delta (\eta_{2}/\sin \Theta)}{\Delta (\cot \Theta)},$$

$$(13)$$

with similar formulæ for  $\gamma_1$ ,  $\gamma_2$ ,  $\delta_1$ ,  $\delta_2$ , where  $\Delta F(\kappa a)$  denotes F(10) - F(9). Also,

$$\frac{\partial \alpha_{1}}{\partial \theta} = \left[ \Delta \left( \frac{\partial \eta_{1}}{\partial \theta} / \sin \theta \right) + \frac{\pi}{180} \sin \frac{1}{2} \theta \left\{ \alpha_{1} + \beta_{1} \Delta \left( \kappa a \cot \theta \right) \right\} \right] / \Delta \left( \cot \theta \right), 
\frac{\partial \beta_{1}}{\partial \theta} = \left[ \Delta \left( \frac{\partial \eta_{1}}{\partial \theta} / \cos \theta \right) - \frac{\pi}{180} \sin \frac{1}{2} \theta \left\{ \beta_{1} + \alpha_{1} \Delta \left( \kappa a \tan \theta \right) \right\} \right] / \Delta \left( \tan \theta \right),$$
(14)

with similar formulæ for the remaining cases.

The values of the functions themselves are given in Table XXIV. for the range  $\theta = 0^{\circ}$  to 150°, and are plotted by means of small circles in figs. 13 to 16. As will be seen, it is possible to draw smooth curves with few undulations approximately through these points. The complete graphs of  $\alpha_1$ ,  $\alpha_2$ , &c., differ from the curves of figs. 13 to 16 by a number of ripples. An attempt has only been made to draw these ripples in those parts of the curves actually required for interpolation. For this the gradients were necessary, and the values of the derivatives used are given in Table XXV. With the limited data of Tables XXIV., XXV. the drawing of the ripples is not perfectly determinate, but it was assumed that the graphs of  $\eta_1$ ,  $\eta_2$ , &c. (and of  $Y_1$ ,  $Y_2$ , &c.), are without ripples, and after a number of trials the ripples of the graphs of  $\alpha_1$ ,  $\alpha_2$ , &c., were drawn in such a way as to secure this, but they are not given in the figures.

TABLE XXIV.

θ.	$\alpha_1$ .	$eta_{1}$ .	a <sub>2</sub> .	$eta_2$ .	γ1•	$\delta_1$ .	$\gamma_2$ .	δ₂.
0 10 20 30	-0.068 -0.036 -0.040 +0.005	+0:007 -0:183 -0:516 -0:459	-0.340 +0.049 +0.308 -0.121	+0.296 +0.285 +0.282 +0.115	+0.068 +0.043 +0.015 +0.022	$ \begin{array}{c} -0.007 \\ +0.051 \\ +0.192 \\ +0.293 \end{array} $	+0.340 $+0.197$ $-0.022$ $-0.056$	$ \begin{array}{r} -0.296 \\ -0.277 \\ -0.261 \\ -0.250 \end{array} $
45	+0.290	-0.129	-0.172	+0.440	-0.035	+0.242	+0.008	-0.190
60 70 80	$ \begin{array}{r} -0.352 \\ -0.469 \\ -0.620 \end{array} $	$     \begin{array}{r}       -0.001 \\       -0.428 \\       -0.938     \end{array} $	+0.116  +0.545  +0.324	+0.648  +0.461  +0.059	$ \begin{array}{r} -0.057 \\ -0.046 \\ -0.039 \end{array} $	+0.187 $+0.140$ $+0.143$	+0.003 $-0.059$ $-0.131$	$-0.250 \\ -0.228 \\ -0.199$
90	-0.144	-1.38	+0.085	-0.291	-0.072	+0.118	-0.187	-0.120
100 110 120	+0.212 +0.960 +1.360	-1.69 $-1.68$ $-1.56$	$     \begin{array}{r}       -0.696 \\       -1.34 \\       -2.31     \end{array} $	$   \begin{array}{r}     -0.272 \\     -0.050 \\     +0.576   \end{array} $	$-0.164 \\ -0.267 \\ -0.505$	+0.116 $+0.041$ $-0.070$	-0.260 $-0.377$ $-0.541$	-0.025 + 0.070 + 0.261
135	+2.23	-1:14	-3.90	+2.28	-0.861	-0.368	-1:26	+0.495
150	+3.30	-0.59	-6.81	+5.83	-1:586	-0.356	-3.20	+1.71

TABLE XXV.

$\theta$ .	$\frac{\partial \alpha_1}{\partial \theta}$ .	$\frac{\partial \beta_1}{\partial \theta}$ .	$\frac{\partial \alpha_2}{\partial \theta}$ .	$\frac{\partial \beta_2}{\partial \theta}$ .	$\frac{\partial \gamma_1}{\partial \theta}$ .	$\frac{\partial \delta_1}{\partial \theta}$ .	$\frac{\partial \gamma_2}{\partial \theta}$ .	$\frac{\partial \delta_2}{\partial \theta}$ .
90 100 110 120 135 150	+0.052 +0.049 +0.066 +0.050 +0.022 +0.034	$ \begin{array}{r} -0.062 \\ -0.009 \\ -0.020 \\ +0.055 \\ +0.049 \\ +0.010 \end{array} $	$ \begin{array}{r} -0.043 \\ -0.082 \\ -0.075 \\ -0.087 \\ -0.148 \\ -0.400 \end{array} $	+0.0032 $-0.0099$ $+0.065$ $+0.056$ $+0.089$ $+0.148$	-0.026 -0.055 -0.027	$ \begin{array}{r} -0.014 \\ -0.005 \\ -0.036 \\ -0.049 \end{array} $	$-0.064 \\ -0.277$	+0.019 +0.023 +0.124

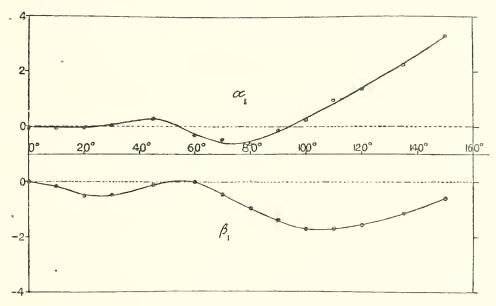


Fig. 13. Table XXIV.

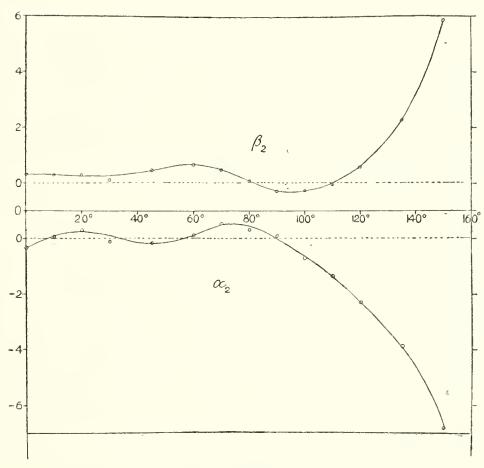


Fig. 14. Table XXIV.

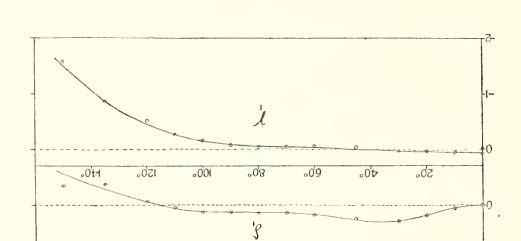


Fig. 15. Table XXIV.

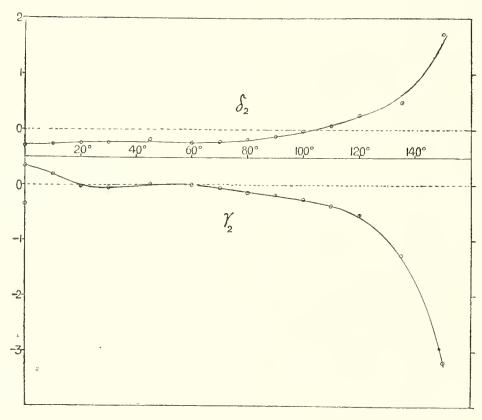


Fig. 16. Table XXIV.

In using the functions  $\alpha_1$ ,  $\alpha_2$ , &c., considerations of the possible forms for the theoretical higher approximations for large values of  $\kappa \alpha$  have been continually in mind. Take  $Y_1$ , for example; the first approximation being  $Y_1 = \frac{1}{2}\kappa \alpha \cos \Theta$ , let us assume an expression of the form

$$Y_1 = A(\theta, \kappa a) \cos \{\Phi(\theta, \kappa a)\} . . . . . . . . (15)$$

Then in the first approximation, we have

$$A(\theta, \kappa a) = \frac{1}{2} \kappa a, \qquad \Phi(\theta, \kappa a) = \Theta.$$

Let us now suppose that higher approximations are got by taking

$$A(\theta, \kappa \alpha) = \frac{1}{2}\kappa \alpha + A_0(\theta) + \frac{A_1(\theta)}{\kappa \alpha}, \qquad \Phi(\theta, \kappa \alpha) = \Theta + \frac{\Phi_1(\theta)}{\kappa \alpha} + \frac{\Phi_2(\theta)}{(\kappa \alpha)^2}, \qquad (16)$$

where the new functions of  $\theta$  are small compared with  $\kappa a$ . The omission of a term independent of  $\kappa a$  in  $\Phi(\theta, \kappa a)$  is necessary if  $Y_1/\frac{1}{2}\kappa a \cos \theta \to 1$  as  $\kappa a \to \infty$ .

To the same order of approximation, (16) yields

$$\eta_1 = \left(\alpha_0 + \frac{\alpha_1}{\kappa \alpha}\right) \cos \Theta + \left(b_0 + \frac{b_1}{\kappa \alpha}\right) \sin \Theta, \quad (17)$$

where  $a_0$ ,  $a_1$ ,  $b_0$ ,  $b_1$  are functions of  $\theta$ , being calculable in terms of those in (16). We then obtain, from (13),

$$a_1 = a_0 + \frac{a_1}{180} \left\{ 19 + \frac{\sin\left(38\cos\frac{1}{2}\theta\right)}{\sin\left(2\cos\frac{1}{2}\theta\right)} \right\} + \frac{b_1}{90} \frac{\sin\left(18\cos\frac{1}{2}\theta\right)\sin\left(20\cos\frac{1}{2}\theta\right)}{\sin\left(2\cos\frac{1}{2}\theta\right)}, \quad (18)$$

and a similar expression for  $\beta_1$ .

It is interesting to compare this hypothetical approximate expression for  $\alpha_1$  with what is known about the exact value of this function. Since the coefficients of  $a_1$  and  $b_1$  in (18) are rapidly oscillating functions of  $\theta$  with small amplitude, the suggestion immediately arises that the smooth curve  $\alpha_1$  of fig. 13 is the graph of  $a_0$ , or perhaps of  $a_0 + \frac{19}{180}a_1$ , and that the ripples of the same figure are approximately represented by the remainder of (18).

From  $\theta = 150^{\circ}$  to  $\theta = 180^{\circ}$  simple graphical interpolation of  $Y_1, Y_2, Z_1, Z_2$  has been relied upon.

Table XXVI. contains all the interpolated values of  $Y_1$ ,  $Y_2$ ,  $Z_1$ ,  $Z_2$ ,  $Y_1^2 + Y_2^2$ ,  $Z_1^2 + Z_2^2$  that have been used.

TABLE XXVI.

	-		$\kappa a = 9.$	•		
$\theta$ .	Y <sub>1</sub>	$Y_2$ .	$Z_1$ .	$Z_2$ .	$Y_1^2 + Y_2^2$ .	$Z_1^2 + Z_2^2$ .
5·81 12·70 17·00	$2 \cdot 893$ $2 \cdot 791$ $2 \cdot 610$	- 3:096 - 3:680 - 4:035	-2.863 $-2.631$ $-2.369$	+ 3·038 + 3·426 + 3·737	$18.0 \\ 21.3 \\ 23.1$	17 · 43 18 · 66 19 · 58
$20 \cdot 42$ $23 \cdot 34$ $25 \cdot 95$	$2 \cdot 361$ $2 \cdot 043$ $1 \cdot 678$	$ \begin{array}{rrrr}  & 4 \cdot 233 \\  & 4 \cdot 337 \\  & 4 \cdot 367 \end{array} $	$-2 \cdot 077 \\ -1 \cdot 760 \\ -1 \cdot 420$	+ 3·992 + 4·191 + 4·343	$23 \cdot 5$ $23 \cdot 0$ $21 \cdot 9$	$20 \cdot 25$ $20 \cdot 66$ $20 \cdot 88$
$28 \cdot 31$ $30 \cdot 50$ $32 \cdot 55$	$1 \cdot 272$ $0 \cdot 830$ $0 \cdot 370$	$\begin{array}{rrr} - & 4 \cdot 360 \\ - & 4 \cdot 333 \\ - & 4 \cdot 284 \end{array}$	-1.059 $-0.683$ $-0.293$	+ 4·449 + 4·513 + 4·540	$20 \cdot 6$ $19 \cdot 5$ $18 \cdot 5$	$20 \cdot 92$ $20 \cdot 83$ $20 \cdot 70$
$34 \cdot 48$ $36 \cdot 30$ $38 \cdot 05$	$ \begin{array}{r} -0.102 \\ -0.562 \\ -1.015 \end{array} $	$ \begin{array}{rrr}     & 4 \cdot 241 \\     & 4 \cdot 182 \\     & 4 \cdot 114 \end{array} $	$+0.102 \\ +0.496 \\ +0.895$	+ 4·532 + 4·488 + 4·412	18·0 17·8 18·0	$20 \cdot 55$ $20 \cdot 39$ $20 \cdot 27$
$39 \cdot 71$ $41 \cdot 32$ $42 \cdot 86$	$ \begin{array}{r} -1.459 \\ -1.878 \\ -2.270 \end{array} $	- 4.036 - 3.960 - 3.875	+1.286 $+1.672$ $+2.045$	+ 4·299 + 4·158 + 3·987	$18 \cdot 4$ $19 \cdot 2$ $20 \cdot 2$	$20 \cdot 13$ $20 \cdot 09$ $20 \cdot 08$
$44 \cdot 36$ $45 \cdot 81$ $47 \cdot 22$	$ \begin{array}{r} -2.623 \\ -2.952 \\ -3.234 \end{array} $	$ \begin{array}{rrr}     - & 3.783 \\     - & 3.641 \\     - & 3.493 \end{array} $	+2.414 $+2.739$ $+3.063$	+ 3.788 + 3.565 + 3.318	$21 \cdot 2$ $22 \cdot 0$ $22 \cdot 7$	20.18 $20.21$ $20.39$
48.58 $49.92$ $51.22$	-3.487 -3.696 -3.869	$\begin{array}{rrrr} - & 3 \cdot 312 \\ - & 3 \cdot 105 \\ - & 2 \cdot 870 \end{array}$	+3.352 $+3.616$ $+3.854$	$\begin{array}{r} + \ 3.047 \\ + \ 2.751 \\ + \ 2.440 \end{array}$	$23 \cdot 1$ $23 \cdot 3$ $23 \cdot 2$	20.52 $20.64$ $20.81$
$52 \cdot 49$ $53 \cdot 73$ $54 \cdot 95$	$ \begin{array}{r} -3.998 \\ -4.081 \\ -4.169 \end{array} $	$\begin{array}{rrrr} - & 2.580 \\ - & 2.251 \\ - & 1.893 \end{array}$	+4.056  +4.225  +4.364	$\begin{array}{c} + 2 \cdot 106 \\ + 1 \cdot 759 \\ + 1 \cdot 396 \end{array}$	$22 \cdot 6$ $21 \cdot 7$ $21 \cdot 0$	20.89 $20.95$ $20.99$
$56 \cdot 14$ $57 \cdot 31$ $58 \cdot 47$	$ \begin{array}{r} -4 \cdot 203 \\ -4 \cdot 207 \\ -4 \cdot 198 \end{array} $	- 1.511 - 1.110 - 0.686	+4.465  +4.531  +4.560	$\begin{array}{c} + \ 1 \cdot 022 \\ + \ 0 \cdot 639 \\ + \ 0 \cdot 250 \end{array}$	$   \begin{array}{c}     19 \cdot 9 \\     18 \cdot 9 \\     18 \cdot 1   \end{array} $	20.98 $20.94$ $20.86$
$60 \cdot 70$ $62 \cdot 86$ $64 \cdot 96$	$     \begin{array}{r}       -4 \cdot 073 \\       -3 \cdot 872 \\       -3 \cdot 581     \end{array} $	+ 0.201  + 1.099  + 2.000	+4.515  +4.330  +4.016	$ \begin{array}{rrr}     & - & 0.535 \\     & - & 1.309 \\     & - & 2.048 \end{array} $	$16 \cdot 6$ $16 \cdot 2$ $16 \cdot 8$	$\begin{array}{c} 20.67 \\ 20.46 \\ 20.32 \end{array}$
67.00 $68.99$ $70.93$	$\begin{array}{c c} -3 \cdot 247 \\ -2 \cdot 873 \\ -2 \cdot 439 \end{array}$	+ 2.826  + 3.551  + 4.137	+3.577  +3.032  +2.395	$ \begin{array}{rrr}     & - & 2 \cdot 733 \\     & - & 3 \cdot 337 \\     & - & 3 \cdot 847 \end{array} $	$18.5 \\ 20.9 \\ 23.1$	$\begin{array}{c} 20 \cdot 26 \\ 20 \cdot 34 \\ 20 \cdot 54 \end{array}$
$72 \cdot 82$ $74 \cdot 68$ $76 \cdot 49$	$ \begin{array}{c c} -1.967 \\ -1.427 \\ -0.829 \end{array} $	+ 4.589 + 4.845 + 4.917	+1.688  +0.930  +0.143	$\begin{array}{rrrr} - & 4 \cdot 234 \\ - & 4 \cdot 498 \\ - & 4 \cdot 615 \end{array}$	$24 \cdot 9$ $25 \cdot 5$ $24 \cdot 9$	20.78 $21.10$ $21.32$
$78 \cdot 26$ $80 \cdot 00$ $81 \cdot 72$	$ \begin{array}{r} -0.217 \\ +0.442 \\ +1.123 \end{array} $	+ 4.820 + 4.554 + 4.123	$ \begin{array}{r} -0.645 \\ -1.418 \\ -2.146 \end{array} $	$ \begin{array}{rrrr}     & - & 4 \cdot 587 \\     & - & 4 \cdot 421 \\     & - & 4 \cdot 109 \end{array} $	$23 \cdot 3$ $21 \cdot 6$ $18 \cdot 3$	21 · 46 21 · 56 21 · 49

Table XXVI. (continued).

$\kappa a = 9.$								
$\theta$ .	$\mathbf{Y}_{1}$ .	Y <sub>2</sub> .	$Z_1$ .	$Z_2$ .	$Y_1^2 + Y_2^2$ .	$Z_1^2 + Z_2^2$ .		
83 · 41 85 · 06 86 · 69	+1.784  +2.415  +3.004	$\begin{array}{r} + \ 3.541 \\ + \ 2.873 \\ + \ 2.116 \end{array}$	$ \begin{array}{r} -2.812 \\ -3.392 \\ -3.872 \end{array} $	$ \begin{array}{rrrr}     & - & 3 \cdot 671 \\     & - & 3 \cdot 116 \\     & - & 2 \cdot 462 \end{array} $	$15 \cdot 7$ $14 \cdot 1$ $13 \cdot 5$	$21 \cdot 38$ $21 \cdot 22$ $21 \cdot 05$		
$88 \cdot 30$ $89 \cdot 88$ $91 \cdot 45$	+3.574 $+4.034$ $+4.410$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{r} -4 \cdot 238 \\ -4 \cdot 477 \\ -4 \cdot 585 \end{array} $	$\begin{array}{cccc} - & 1.727 \\ - & 0.934 \\ - & 0.108 \end{array}$	$14.5 \\ 16.5 \\ 19.5$	$20 \cdot 94$ $20 \cdot 92$ $21 \cdot 03$		
$92 \cdot 99$ $94 \cdot 51$ $96 \cdot 01$	4 · 68 4 · 81 4 · 81	$\begin{array}{c c} - 1.03 \\ - 1.71 \\ - 2.31 \end{array}$	$     \begin{array}{r}       -4 \cdot 552 \\       -4 \cdot 380 \\       -4 \cdot 068     \end{array} $	$0.729 \\ 1.540 \\ 2.300$	$23 \cdot 0 \\ 26 \cdot 1 \\ 28 \cdot 5$	$21 \cdot 25$ $21 \cdot 56$ $21 \cdot 84$		
97.50 $98.97$ $100.42$	$4.65 \\ 4.31 \\ 3.84$	$\begin{array}{ c c c c c }\hline & - & 2 \cdot 78 \\ & - & 3 \cdot 16 \\ & - & 3 \cdot 41 \\ \hline\end{array}$	$ \begin{array}{r} -3.632 \\ -3.081 \\ -2.431 \end{array} $	$3 \cdot 006$ $3 \cdot 615$ $4 \cdot 112$	$29 \cdot 4 \\ 28 \cdot 6 \\ 26 \cdot 4$	$22 \cdot 23$ $22 \cdot 56$ $22 \cdot 82$		
$101 \cdot 86$ $103 \cdot 29$ $104 \cdot 70$	$ \begin{array}{r} 3 \cdot 21 \\ 2 \cdot 48 \\ 1 \cdot 62 \end{array} $	$ \begin{array}{rrr}     - & 3 \cdot 57 \\     - & 3 \cdot 59 \\     - & 3 \cdot 51 \end{array} $	$ \begin{array}{r} -1.709 \\ -0.923 \\ -0.100 \end{array} $	4·485 4·716 4·800	$23 \cdot 1$ $19 \cdot 0$ $14 \cdot 9$	$23 \cdot 04$ $23 \cdot 09$ $23 \cdot 05$		
$106 \cdot 09$ $107 \cdot 48$ $108 \cdot 85$	$ \begin{array}{r} 0.71 \\ -0.27 \\ -1.25 \end{array} $	$\begin{array}{ c c c c c }\hline & - & 3 \cdot 32 \\ & - & 3 \cdot 07 \\ & - & 2 \cdot 75 \\ \hline\end{array}$	+0.735 $1.556$ $2.324$	$4 \cdot 734$ $4 \cdot 527$ $4 \cdot 177$	$   \begin{array}{c}     11.5 \\     9.5 \\     9.1   \end{array} $	$22 \cdot 95$ $22 \cdot 92$ $22 \cdot 85$		
$110 \cdot 21$ $111 \cdot 56$ $112 \cdot 90$	$ \begin{array}{r} -2 \cdot 27 \\ -3 \cdot 17 \\ -3 \cdot 98 \end{array} $	$ \begin{array}{rrrr}  & - & 2 \cdot 39 \\  & - & 1 \cdot 99 \\  & - & 1 \cdot 60 \end{array} $	3·040 3·661 4·181	$3 \cdot 694 \\ 3 \cdot 078 \\ 2 \cdot 360$	10·9 14·0 18·4	$22 \cdot 89$ $22 \cdot 88$ $23 \cdot 05$		
. 114·22 115·54 116·85	$ \begin{array}{r} -4.72 \\ -5.31 \\ -5.75 \end{array} $	$ \begin{array}{rrrr}  & - & 1 \cdot 19 \\  & - & 0 \cdot 79 \\  & - & 0 \cdot 41 \end{array} $	4.580 $4.834$ $4.937$	$ \begin{array}{r} 1 \cdot 559 \\ 0 \cdot 704 \\ - 0 \cdot 170 \end{array} $	$23 \cdot 7$ $28 \cdot 8$ $33 \cdot 2$	$23 \cdot 41$ $23 \cdot 86$ $24 \cdot 40$		
$118 \cdot 15$ $119 \cdot 44$ $120 \cdot 73$	$     \begin{array}{r}       -5 \cdot 99 \\       -6 \cdot 04 \\       -5 \cdot 88     \end{array} $	$\begin{array}{c} -0.07 \\ +0.25 \\ 0.52 \end{array}$	4.879 $4.669$ $4.31$	$\begin{array}{rrrr} - & 1.052 \\ - & 1.905 \\ - & 2.76 \end{array}$	35 · 9 36 · 5 34 · 8	$24 \cdot 91$ $25 \cdot 43$ $26 \cdot 2$		
$122 \cdot 00$ $123 \cdot 27$ $124 \cdot 53$	$     \begin{array}{r}       -5 \cdot 54 \\       -5 \cdot 01 \\       -4 \cdot 31   \end{array} $	$0.76 \\ 0.93 \\ 1.10$	$3.82 \\ 3.17 \\ 2.42$	$\begin{array}{rrrr} - & 3 \cdot 50 \\ - & 4 \cdot 16 \\ - & 4 \cdot 67 \end{array}$	$ \begin{array}{c} 31 \cdot 3 \\ 26 \cdot 0 \\ 19 \cdot 8 \end{array} $	$26 \cdot 8$ $27 \cdot 4$ $27 \cdot 7$		
$125 \cdot 78$ $127 \cdot 02$ $128 \cdot 26$	$egin{array}{l} -3 \cdot 46 \ -2 \cdot 47 \ -1 \cdot 37 \end{array}$	$1 \cdot 24$ $1 \cdot 41$ $1 \cdot 55$	$1.59 \\ 0.70 \\ -0.21$	$ \begin{array}{rrr}     - & 5 \cdot 06 \\     - & 5 \cdot 31 \\     - & 5 \cdot 40 \end{array} $	13.5. 8.1 4.3	$28 \cdot 1 \\ 28 \cdot 7 \\ 29 \cdot 2$		
$129 \cdot 49$ $130 \cdot 72$ $131 \cdot 94$	$-0.20 \\ +1.02 \\ 2.22$	1.67 $1.83$ $1.95$	$     \begin{array}{r}       -1 \cdot 10 \\       -1 \cdot 99 \\       -2 \cdot 84   \end{array} $	$ \begin{array}{rrr}     - & 5 \cdot 30 \\     - & 5 \cdot 05 \\     - & 4 \cdot 62 \end{array} $	$\begin{array}{c} 2 \cdot 8 \\ 4 \cdot 4 \\ 8 \cdot 7 \end{array}$	$29 \cdot 3$ $29 \cdot 5$ $29 \cdot 4$		
133 · 15 134 · 36 135 · 56	$3 \cdot 36 \\ 4 \cdot 39 \\ 5 \cdot 31$	$2 \cdot 05$ $2 \cdot 15$ $2 \cdot 28$	$   \begin{array}{r}     -3 \cdot 63 \\     -4 \cdot 30 \\     -4 \cdot 85   \end{array} $	$ \begin{array}{rrrr}  & - & 4 \cdot 04 \\  & - & 3 \cdot 31 \\  & - & 2 \cdot 47 \end{array} $	$15 \cdot 5$ $23 \cdot 9$ $33 \cdot 4$	$29 \cdot 5$ $29 \cdot 5$ $29 \cdot 6$		

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Table XXVI. (continued).

$\kappa a = 9.$							
θ.	Y <sub>1</sub> .	$Y_2$ .	$Z_1$ .	$Z_2$ .	$Y_1^2 + Y_2^2$ .	$Z_{1}^{2} + Z_{2}^{2}$	
136.76 $137.95$ $139.14$	6 · 02 6 · 56 6 · 89	$2.55 \\ 2.77 \\ 3.00$	$   \begin{array}{r}     -5 \cdot 27 \\     -5 \cdot 52 \\     -5 \cdot 60   \end{array} $	$ \begin{array}{rrrr}  & - & 1 \cdot 49 \\  & - & 0 \cdot 44 \\  & + & 0 \cdot 67 \end{array} $	$42 \cdot 7$ $50 \cdot 7$ $56 \cdot 5$	30·0 30·7 31·8	
$140 \cdot 32 \\ 141 \cdot 50 \\ 142 \cdot 68$	6 · 99 6 · 90 6 · 56	3·16 3·35 3·41	-5.52 $-5.29$ $-4.85$	$     \begin{array}{r}       1 \cdot 81 \\       2 \cdot 93 \\       4 \cdot 04     \end{array} $	58·9 58·8 54·7	33·8 36·6 39·8	
143.85 145.01 146.18	$6 \cdot 04 \\ 5 \cdot 29 \\ 4 \cdot 33$	$3 \cdot 40 \\ 3 \cdot 33 \\ 3 \cdot 16$	$ \begin{array}{r} -4 \cdot 23 \\ -3 \cdot 49 \\ -2 \cdot 62 \end{array} $	5 · 02 5 · 90 6 · 65	$48 \cdot 0$ $39 \cdot 1$ $28 \cdot 7$	43·1 47·0 51·1	
$147 \cdot 33$ $148 \cdot 49$ $149 \cdot 65$	3·19 1·93 0·58	$2.88 \\ 2.45 \\ 1.97$	$     \begin{array}{r}       -1.68 \\       -0.67 \\       +0.36     \end{array} $	$7 \cdot 17 \\ 7 \cdot 52 \\ 7 \cdot 62$	$18.5 \\ 9.7 \\ 4.2$	54·2 57·0 58·2	
150 · 2 150 · 4 150 · <b>6</b> 150 · 8	$ \begin{array}{r} -2.50 \\ -4.82 \\ -6.81 \\ -8.17 \end{array} $	$ \begin{array}{r} 0.5 \\ -1.2 \\ -3.6 \\ -6.5 \end{array} $	$ \begin{array}{c} 2 \cdot 6 \\ 4 \cdot 4 \\ 6 \cdot 02 \\ 7 \cdot 28 \end{array} $	$7 \cdot 1 \\ 5 \cdot 7 \\ 3 \cdot 6 \\ 0 \cdot 5$	6.5 $24.6$ $59.4$ $109$	57 52 49 53	
160·2 160·4 160·6 160·8	$ \begin{array}{r}  -9.58 \\  -9.30 \\  -8.42 \\  -6.98 \end{array} $	$\begin{array}{r} -14 \cdot 2 \\ -18 \cdot 1 \\ -22 \cdot 4 \\ -26 \cdot 9 \end{array}$	$8 \cdot 32$ $8 \cdot 18$ $7 \cdot 60$ $6 \cdot 36$	$ \begin{array}{r} -8.1 \\ -12.8 \\ -17.9 \\ -23.1 \end{array} $	294 415 573 773	135 231 378 574	
$170 \cdot 2$ $170 \cdot 4$ $170 \cdot 6$ $170 \cdot 8$	$ \begin{array}{r} -3 \cdot 20 \\ -1 \cdot 20 \\ 0 \cdot 00 \\ 0 \cdot 60 \end{array} $	$ \begin{array}{r} -34 \cdot 8 \\ -38 \cdot 0 \\ -40 \cdot 2 \\ -41 \cdot 5 \end{array} $	3.60 $2.18$ $1.36$ $0.82$	$ \begin{array}{r} -33 \cdot 0 \\ -37 \cdot 2 \\ -40 \cdot 0 \\ -41 \cdot 3 \end{array} $	$1220 \\ 1445 \\ 1620 \\ 1720$	1100 1390 1600 1710	

$\kappa u = 10.$								
θ.	Y <sub>1</sub> .	Y <sub>2</sub> .	$Z_1$ .	$Z_2$ .	$Y_1^2 + Y_2^2$ .	$Z_1^2 + Z_2^2$ .		
$ \begin{array}{c}                                     $	$2 \cdot 28$ $2 \cdot 53$ $2 \cdot 80$ $3 \cdot 12$ $3 \cdot 44$ $3 \cdot 75$ $4 \cdot 07$ $4 \cdot 36$	4.59 $4.51$ $4.26$ $3.91$ $3.48$ $3.03$ $2.58$ $2.15$	$ \begin{array}{r} -2 \cdot 085 \\ -2 \cdot 420 \\ -2 \cdot 750 \end{array} $ $ \begin{array}{r} -3 \cdot 066 \\ -3 \cdot 369 \\ -3 \cdot 656 \end{array} $ $ \begin{array}{r} -3 \cdot 924 \\ -4 \cdot 168 \\ -4 \cdot 386 \end{array} $	$ \begin{array}{rrrr}     & 4 \cdot 376 \\     & 4 \cdot 330 \\     & 4 \cdot 197 \end{array} $ $ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$26 \cdot 3$ $26 \cdot 7$ $26 \cdot 0$ $25 \cdot 0$ $23 \cdot 9$ $23 \cdot 2$ $23 \cdot 1$ $23 \cdot 5$	$23 \cdot 60$ $24 \cdot 61$ $25 \cdot 17$ $25 \cdot 42$ $25 \cdot 42$ $25 \cdot 30$ $25 \cdot 12$ $24 \cdot 93$ $24 \cdot 81$		

Table XXVI. (continued).

$\kappa a = 10.$								
$\theta$ .	Y <sub>1</sub> .	${ m Y}_2.$	$Z_1$ .	$Z_2$ .	$Y_1^2 + Y_2^2$ .	$Z_1^2 + Z_2^2$ .		
32.55 $34.29$ $35.95$	$4 \cdot 64 \\ 4 \cdot 87 \\ 5 \cdot 06$	1·72 1·27 0·86	-4.577 $-4.738$ $-4.863$	- 1·945 - 1·520 - 1·085	$24 \cdot 5$ $25 \cdot 3$ $26 \cdot 3$	$24 \cdot 73$ $24 \cdot 76$ $24 \cdot 83$		
$37 \cdot 53$ $39 \cdot 06$ $41 \cdot 95$	$5 \cdot 20$ $5 \cdot 27$ $5 \cdot 24$	$0.47 \\ 0.10 \\ -0.69$	$-4 \cdot 956 \\ -5 \cdot 009 \\ -4 \cdot 993$	- 0.644 - 0.200 0.678	$27 \cdot 3$ $27 \cdot 8$ $27 \cdot 9$	$24 \cdot 98$ $25 \cdot 13$ $25 \cdot 39$		
$44 \cdot 66 $ $47 \cdot 22$ $49 \cdot 66$	$5 \cdot 02$ $4 \cdot 59$ $3 \cdot 96$	$\begin{array}{rrr} - & 1 \cdot 26 \\ - & 1 \cdot 94 \\ - & 2 \cdot 63 \end{array}$	-4.825 $-4.498$ $-4.029$	$ \begin{array}{r} 1 \cdot 530 \\ 2 \cdot 328 \\ 3 \cdot 049 \end{array} $	$26 \cdot 8$ $24 \cdot 8$ $22 \cdot 6$	$25 \cdot 62$ $25 \cdot 65$ $25 \cdot 53$		
$51 \cdot 99$ $54 \cdot 22$ $56 \cdot 38$	$3 \cdot 21$ $2 \cdot 45$ $1 \cdot 64$	$ \begin{array}{rrr}     - & 3 \cdot 27 \\     - & 3 \cdot 86 \\     - & 4 \cdot 43 \end{array} $	$-3 \cdot 430 \\ -2 \cdot 720 \\ -1 \cdot 926$	3.680 $4.200$ $4.604$	$21 \cdot 0$ $20 \cdot 9$ $22 \cdot 3$	$25 \cdot 31$ $25 \cdot 04$ $24 \cdot 90$		
$58 \cdot 46$ $60 \cdot 48$ $62 \cdot 43$	$ \begin{array}{r} 0.82 \\ 0.00 \\ -0.77 \end{array} $	$ \begin{array}{rrrr}  & - & 4 \cdot 85 \\  & - & 5 \cdot 14 \\  & - & 5 \cdot 30 \end{array} $	-1.068 $-0.181$ $+0.708$	4.878 $5.000$ $4.969$	$24 \cdot 2 \\ 26 \cdot 4 \\ 28 \cdot 7$	$24 \cdot 87$ $25 \cdot 03$ $25 \cdot 19$		
$64 \cdot 34$ $66 \cdot 19$ $68 \cdot 00$	$ \begin{array}{rrr}  & - & 1 \cdot 48 \\  & - & 2 \cdot 12 \\  & - & 2 \cdot 65 \end{array} $	$ \begin{array}{rrr}  & 5 \cdot 28 \\  & 5 \cdot 01 \\  & 4 \cdot 55 \end{array} $	+1.577 $2.390$ $3.133$	$4 \cdot 790 \\ 4 \cdot 470 \\ 4 \cdot 006$	$30 \cdot 1$ $29 \cdot 6$ $27 \cdot 7$	$\begin{array}{c} 25 \cdot 43 \\ 25 \cdot 69 \\ 25 \cdot 87 \end{array}$		
$69 \cdot 77$ $71 \cdot 50$ $73 \cdot 19$	$\begin{array}{rrrr} - & 3 \cdot 22 \\ - & 3 \cdot 64 \\ - & 3 \cdot 98 \end{array}$	$\begin{array}{r rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$3 \cdot 777 \\ 4 \cdot 300 \\ 4 \cdot 698$	$3 \cdot 425$ $2 \cdot 731$ $1 \cdot 949$	$25 \cdot 7$ $23 \cdot 2$ $20 \cdot 8$	$26 \cdot 00$ $25 \cdot 95$ $25 \cdot 87$		
74.85 $76.48$ $79.68$	$ \begin{array}{rrrr}     - & 4 \cdot 22 \\     - & 4 \cdot 39 \\     - & 4 \cdot 45 \end{array} $	$ \begin{array}{rrr}  & - & 1 \cdot 25 \\  & - & 0 \cdot 23 \\  & + & 1 \cdot 76 \end{array} $	$4 \cdot 943 \\ 5 \cdot 044 \\ 4 \cdot 786$	$ \begin{array}{r} 1 \cdot 101 \\ 0 \cdot 216 \\ - 1 \cdot 569 \end{array} $	$19 \cdot 4$ $19 \cdot 3$ $22 \cdot 9$	$25 \cdot 64$ $25 \cdot 49$ $25 \cdot 37$		
$82 \cdot 74 \\ 85 \cdot 72 \\ 88 \cdot 62$	$ \begin{array}{rrr}     & - & 4 \cdot 21 \\     & - & 3 \cdot 38 \\     & - & 2 \cdot 04 \end{array} $	$3 \cdot 41$ $4 \cdot 60$ $5 \cdot 11$	$3 \cdot 950$ $2 \cdot 633$ $0 \cdot 998$	$\begin{array}{rrrr} - & 3 \cdot 166 \\ - & 4 \cdot 385 \\ - & 5 \cdot 074 \end{array}$	$29 \cdot 6$ $32 \cdot 6$ $30 \cdot 3$	$\begin{array}{c} 25 \cdot 62 \\ 26 \cdot 16 \\ 26 \cdot 75 \end{array}$		
$91 \cdot 45 \\ 94 \cdot 21 \\ 96 \cdot 91$	$ \begin{array}{rrr}  & - & 0.59 \\  & + & 1.13 \\  & 2.83 \end{array} $	$4 \cdot 87  4 \cdot 03  2 \cdot 75$	-0.767 $-2.457$ $-3.861$	$\begin{array}{rrr} - & 5 \cdot 139 \\ - & 4 \cdot 560 \\ - & 3 \cdot 414 \end{array}$	$24 \cdot 1 \\ 17 \cdot 5 \\ 15 \cdot 6$	$27 \cdot 00$ $26 \cdot 83$ $26 \cdot 58$		
99.56 $102.15$ $104.70$	$4 \cdot 31 \\ 5 \cdot 37 \\ 5 \cdot 77$	$egin{array}{ccc} 1 \cdot 24 \\ - & 0 \cdot 30 \\ - & 1 \cdot 62 \end{array}$	$ \begin{array}{r} -4.809 \\ -5.184 \\ -4.919 \end{array} $	$\begin{array}{c} -1.824 \\ 0.000 \\ 1.840 \end{array}$	$20 \cdot 1 \\ 28 \cdot 9 \\ 35 \cdot 9$	$26 \cdot 46$ $26 \cdot 87$ $27 \cdot 59$		
$107 \cdot 20$ $109 \cdot 67$ $112 \cdot 10$	$5 \cdot 44 \\ 4 \cdot 42 \\ 2 \cdot 74$	$\begin{array}{rrr} - & 2 \cdot 62 \\ - & 3 \cdot 25 \\ - & 3 \cdot 39 \end{array}$	-4.050 $-2.660$ $-0.919$	$3 \cdot 455$ $4 \cdot 688$ $5 \cdot 336$	$36 \cdot 5$ $30 \cdot 1$ $19 \cdot 0$	28 · 34 29 · 06 29 · 31		
114·49 116·85 119·18	$ \begin{array}{r} 0.63 \\ - 1.65 \\ - 3.82 \end{array} $	$ \begin{array}{rrr}     - & 3 \cdot 23 \\     - & 2 \cdot 81 \\     - & 2 \cdot 18 \end{array} $	+0.972 $2.761$ $4.245$	5·343 4·682 3·418	$10.9 \\ 10.6 \\ 19.3$	$ \begin{array}{r} 29 \cdot 49 \\ 29 \cdot 54 \\ 29 \cdot 70 \end{array} $		

Table XXVI. (continued).

	$\kappa a = 10.$							
$\theta$ .	Y <sub>1</sub> .	$Y_2$ .	$Z_1$ .	$Z_2$ .	$Y_1^2 + Y_2^2$ .	$Z_1^2 + Z_2^2$ .		
$ \begin{array}{c}       0.000000000000000000000000000000$	- 5.55 - 6.60 - 6.83	$ \begin{array}{rrrr}  & - & 1 \cdot 31 \\  & - & 0 \cdot 74 \\  & - & 0 \cdot 50 \end{array} $	5 · 243 5 · 585 5 · 511	+ 1.61 - 0.31 - 1.30	$32 \cdot 5$ $44 \cdot 1$ $46 \cdot 9$	$30 \cdot 1$ $31 \cdot 3$ $32 \cdot 1$		
$126 \cdot 03$ $127 \cdot 15$ $128 \cdot 26$	$ \begin{array}{rrr}     - & 6 \cdot 84 \\     - & 6 \cdot 64 \\     - & 6 \cdot 20 \end{array} $	$\begin{array}{c c} - & 0.18 \\ + & 0.07 \\ + & 0.26 \end{array}$	$5 \cdot 240$ $4 \cdot 795$ $4 \cdot 179$	$ \begin{array}{rrr}     & - & 2 \cdot 29 \\     & - & 3 \cdot 23 \\     & - & 4 \cdot 08 \end{array} $	$47 \cdot 1 \\ 44 \cdot 1 \\ 38 \cdot 5$	$32 \cdot 7$ $33 \cdot 4$ $34 \cdot 1$		
$129 \cdot 37$ $130 \cdot 47$ $131 \cdot 57$	$\begin{array}{rrrr} - & 5 \cdot 54 \\ - & 4 \cdot 67 \\ - & 3 \cdot 63 \end{array}$	+ 0.48 + 0.70 + 0.91	$3 \cdot 462$ $2 \cdot 601$ $1 \cdot 662$	$ \begin{array}{rrr}  & -4.82 \\  & -5.42 \\  & -5.84 \end{array} $	$30 \cdot 9$ $22 \cdot 3$ $14 \cdot 0$	$   \begin{array}{r}     35 \cdot 2 \\     36 \cdot 2 \\     36 \cdot 9   \end{array} $		
$132 \cdot 66$ $133 \cdot 75$ $134 \cdot 84$	$\begin{array}{rrrr} - & 2 \cdot 47 \\ - & 1 \cdot 20 \\ + & 0 \cdot 03 \end{array}$	$\begin{array}{c} + \ 1 \cdot 03 \\ + \ 1 \cdot 33 \\ 1 \cdot 49 \end{array}$	$0.664 \\ -0.358 \\ -1.375$	- 6.09 - 6.18 - 6.06	$\begin{array}{c} 7 \cdot 2 \\ 3 \cdot 2 \\ 2 \cdot 2 \end{array}$	37·5 38·2 38·6		
$135 \cdot 92 \\ 137 \cdot 00 \\ 138 \cdot 07$	$1 \cdot 42$ $2 \cdot 74$ $3 \cdot 98$	$egin{array}{c} 1 \cdot 76 \ 1 \cdot 99 \ 2 \cdot 24 \end{array}$	$-2 \cdot 372$ $-3 \cdot 320$ $-4 \cdot 178$	$\begin{array}{r} -5.76 \\ -5.26 \\ -4.57 \end{array}$	$5 \cdot 1$ $11 \cdot 5$ $20 \cdot 9$	38·8 38·7 38·4		
$139 \cdot 14$ $140 \cdot 21$ $141 \cdot 27$	$ 5 \cdot 09 \\ 6 \cdot 02 \\ 6 \cdot 79 $	$ \begin{array}{c c} 2 \cdot 45 \\ 2 \cdot 77 \\ 3 \cdot 10 \end{array} $	$\begin{array}{r} -4.912 \\ -5.501 \\ -5.926 \end{array}$	$\begin{array}{r rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$31 \cdot 9$ $44 \cdot 5$ $55 \cdot 7$	$\begin{array}{c} 37 \cdot 8 \\ 37 \cdot 5 \\ 37 \cdot 6 \end{array}$		
$142 \cdot 33$ $143 \cdot 38$ $144 \cdot 43$	$7 \cdot 35$ $7 \cdot 73$ $7 \cdot 87$	$   \begin{array}{r}     3 \cdot 42 \\     3 \cdot 78 \\     4 \cdot 01   \end{array} $	$     \begin{array}{r}       -6 \cdot 173 \\       -6 \cdot 236 \\       -6 \cdot 112     \end{array} $	$\begin{array}{ccc} - & 0 \cdot 32 \\ + & 1 \cdot 00 \\ & 2 \cdot 32 \end{array}$	$65 \cdot 7 \\ 74 \cdot 0 \\ 78 \cdot 0$	$   \begin{array}{r}     38 \cdot 2 \\     39 \cdot 9 \\     43 \cdot 7   \end{array} $		
$145 \cdot 48$ $146 \cdot 53$ $147 \cdot 57$	$7 \cdot 72$ $7 \cdot 33$ $6 \cdot 64$	$   \begin{array}{r}     4 \cdot 29 \\     4 \cdot 41 \\     4 \cdot 46   \end{array} $	-5.816 $-5.358$ $-4.736$	$3 \cdot 63$ $4 \cdot 88$ $6 \cdot 00$	$78 \cdot 0$ $73 \cdot 2$ $64 \cdot 0$	$47 \cdot 0$ $52 \cdot 5$ $58 \cdot 4$		
$148 \cdot 61 \\ 149 \cdot 65$	5.75 $4.64$	$\frac{4\cdot 40}{4\cdot 20}$	$-3 \cdot 934 \\ -2 \cdot 982$	$6 \cdot 96 \\ 7 \cdot 75$	$52 \cdot 4 \\ 39 \cdot 2$	63·9 69·0		
151 152 153 154 155 156 157 158 159	$   \begin{array}{r}     3 \cdot 00 \\     1 \cdot 78 \\     0 \cdot 19 \\     -1 \cdot 32 \\     -2 \cdot 74 \\     -4 \cdot 02 \\     -5 \cdot 32 \\     -6 \cdot 72 \\     -7 \cdot 78   \end{array} $	$3 \cdot 80$ $3 \cdot 29$ $2 \cdot 62$ $1 \cdot 80$ $0 \cdot 83$ $-0 \cdot 39$ $-1 \cdot 73$ $-3 \cdot 59$ $-5 \cdot 50$	$\begin{array}{c c} -1.50 \\ -0.34 \\ 1.00 \\ 2.20 \\ 3.30 \\ 4.50 \\ 5.44 \\ 6.40 \\ 7.27 \end{array}$	$8 \cdot 68$ $9 \cdot 00$ $9 \cdot 15$ $8 \cdot 93$ $8 \cdot 40$ $7 \cdot 53$ $6 \cdot 22$ $4 \cdot 33$ $2 \cdot 60$	$23 \cdot 1$ $14 \cdot 0$ $6 \cdot 9$ $5 \cdot 0$ $7 \cdot 2$ $16 \cdot 3$ $31 \cdot 3$ $58 \cdot 1$ $90 \cdot 8$	$77 \cdot 6$ $81 \cdot 1$ $84 \cdot 7$ $84 \cdot 5$ $81 \cdot 5$ $77 \cdot 0$ $68 \cdot 3$ $59 \cdot 7$ $59 \cdot 7$		
$162 \\ 164 \\ 166 \\ 168$	$ \begin{array}{r} -10.62 \\ -10.96 \\ -10.58 \\ -9.00 \end{array} $	$ \begin{array}{r} -12 \cdot 45 \\ -18 \cdot 2 \\ -23 \cdot 5 \\ -29 \cdot 5 \end{array} $	$   \begin{array}{c}     9 \cdot 17 \\     9 \cdot 5 \\     9 \cdot 1 \\     7 \cdot 9   \end{array} $	$ \begin{array}{r} -4.80 \\ -11.0 \\ -17.3 \\ -24.8 \end{array} $	268 $451$ $664$ $951$	107 210 380 680		
172 $174$ $176$ $178$	$ \begin{array}{rrr}  & - & 4.76 \\  & - & 2.33 \\  & - & 0.23 \\  & + & 0.60 \end{array} $	$     \begin{array}{r}       -41 \cdot 0 \\       -45 \cdot 6 \\       -49 \cdot 3 \\       -51 \cdot 0     \end{array} $	$ \begin{array}{c c} 4 \cdot 7 \\ 3 \cdot 0 \\ 1 \cdot 6 \\ 0 \cdot 8 \end{array} $	$ \begin{array}{r} -38 \cdot 0 \\ -43 \cdot 9 \\ -48 \cdot 4 \\ -51 \cdot 0 \end{array} $	$   \begin{array}{c}     1700 \\     2080 \\     2430 \\     2600   \end{array} $	$ \begin{array}{r} 1470 \\ 1940 \\ 2350 \\ 2600 \end{array} $		

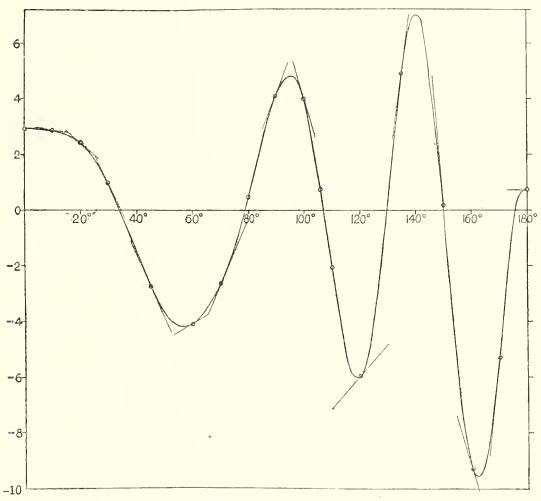


Fig. 17. Tables X., XVIII., XXVI. ( $\kappa a = 9$ ) Y<sub>1</sub>.

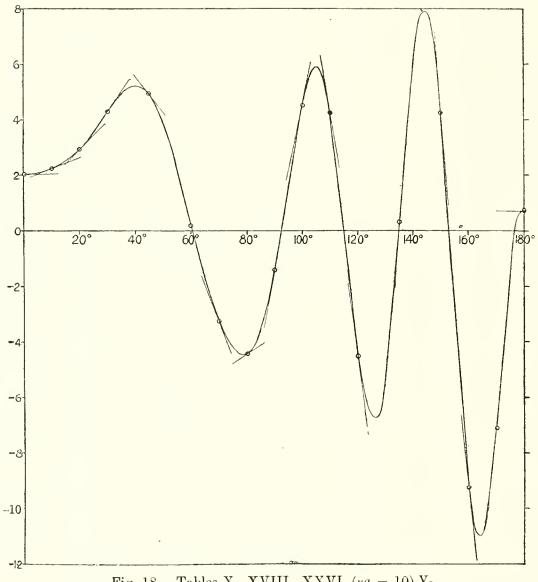


Fig. 18. Tables X., XVIII., XXVI. ( $\kappa a = 10$ ) Y<sub>1</sub>.

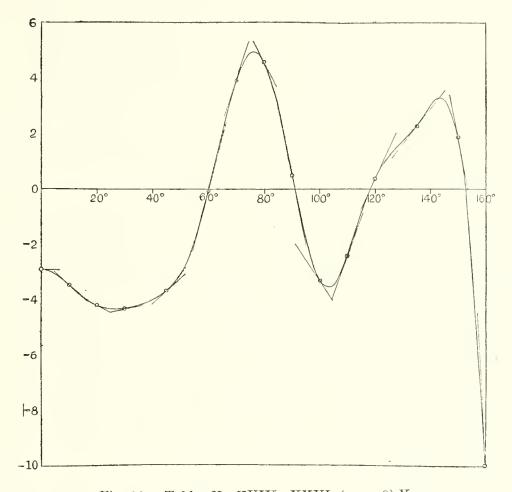


Fig. 19. Tables X., XVIII., XXVI. ( $\kappa a = 9$ ) Y<sub>2</sub>.

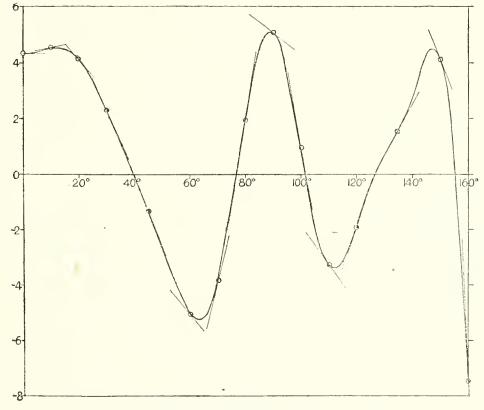


Fig. 20. Tables X., XVIII., XXVI ( $\kappa a = 10$ ) Y<sub>2</sub>.

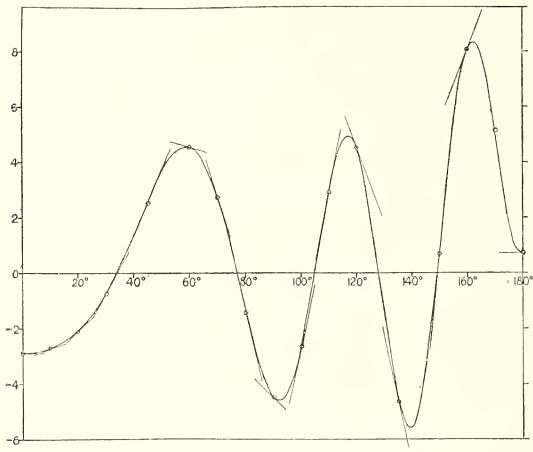


Fig. 21. Tables X., XVIII., XXVI. ( $\kappa a = 9$ ) Z<sub>1</sub>.

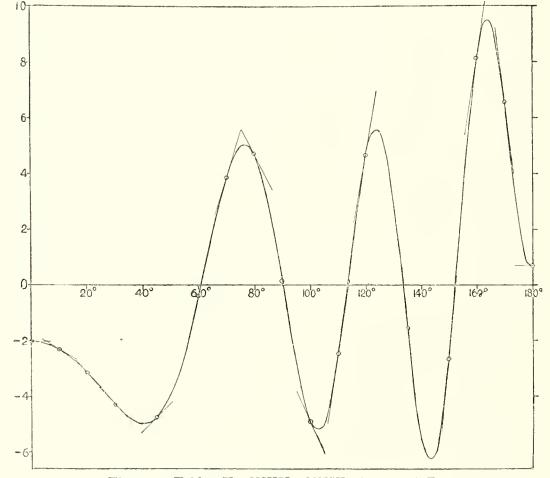


Fig. 22. Tables X., XVIII., XXVI. ( $\kappa a = 10$ ) Z<sub>1</sub>.

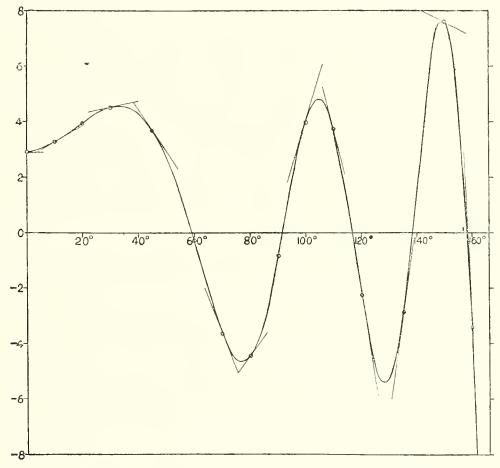


Fig. 23. Tables X., XVIII., XXVI. ( $\kappa a = 9$ ) Z<sub>2</sub>.

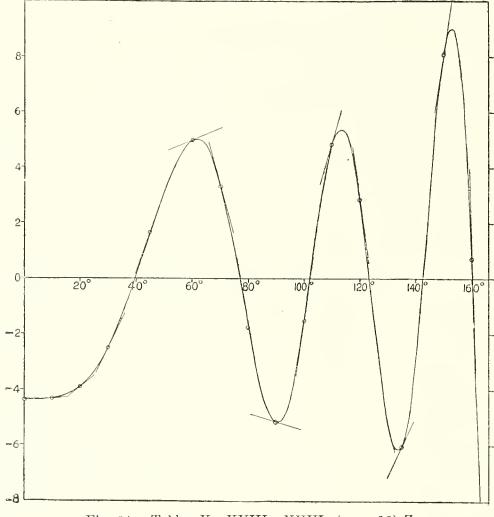
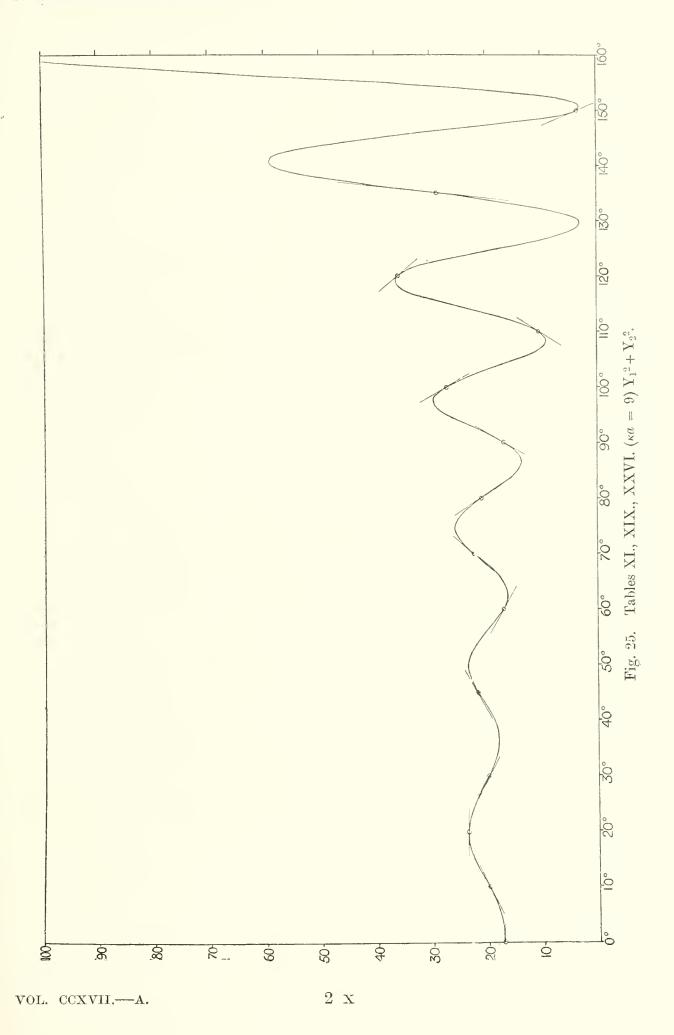


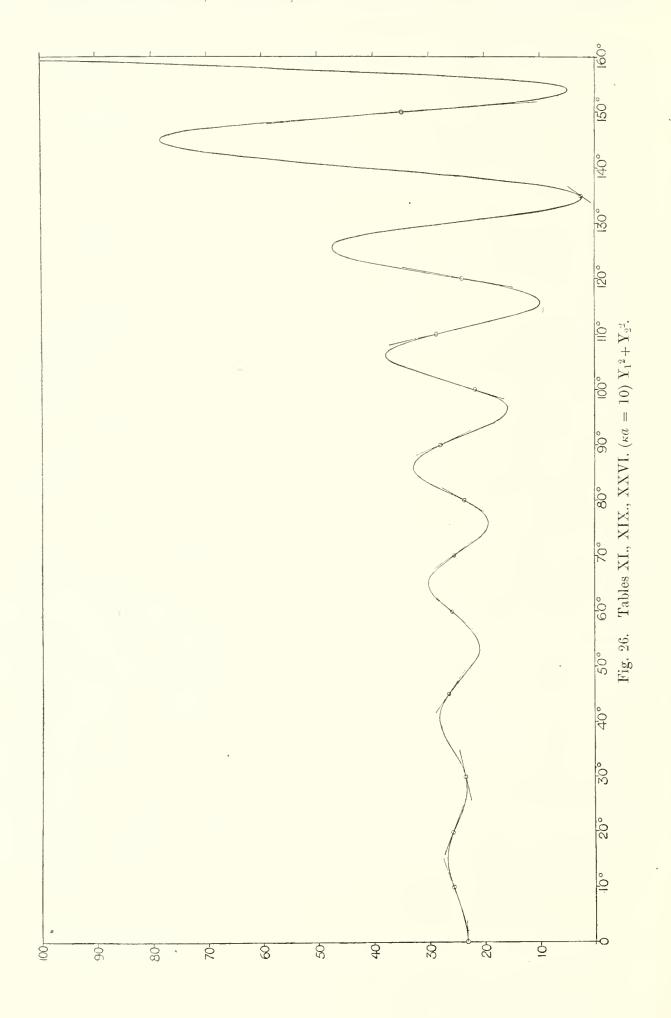
Fig. 24. Tables X., XVIII., XXVI. ( $\kappa a = 10$ ) Z<sub>2</sub>.

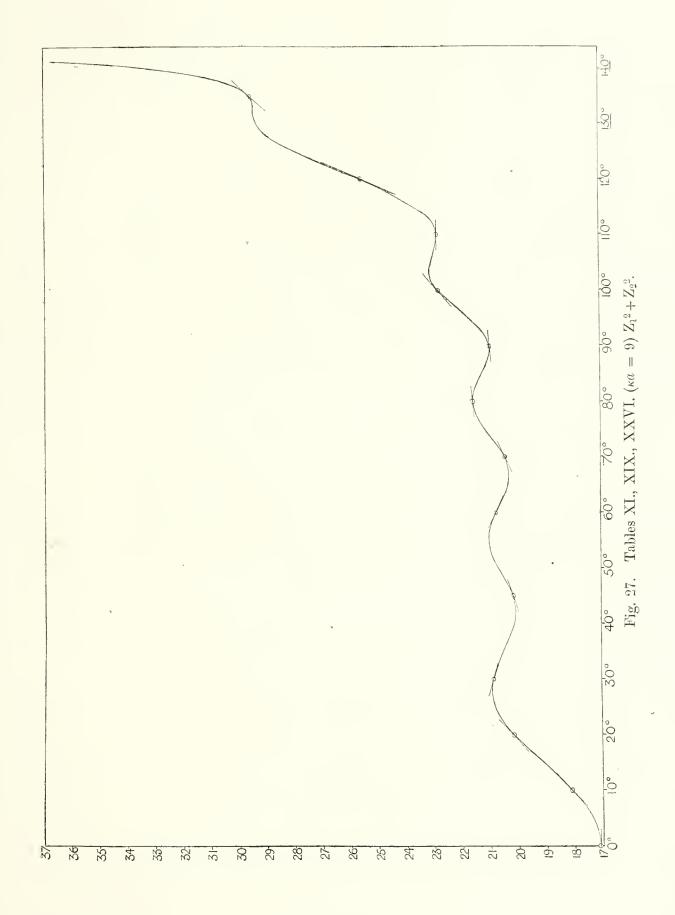
Figs. 25 to 28 give the final graphs of  $Y_1^2 + Y_2^2$ ,  $Z_1^2 + Z_2^2$ , the obtaining of which has been the object of the whole work.

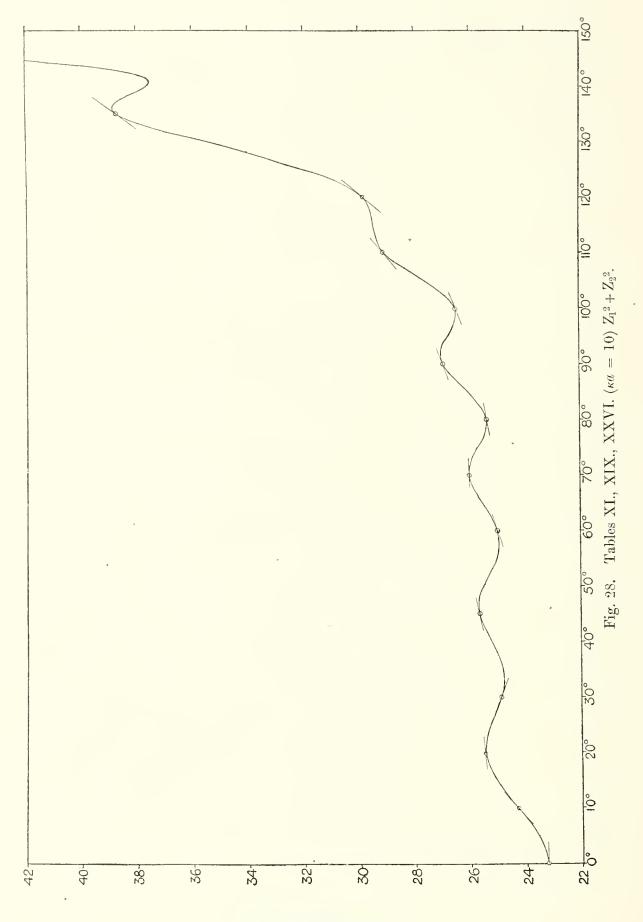
From  $\theta = 0^{\circ}$  to 120° the curve for  $Z_1^2 + Z_2^2$  is probably correct to 0.2 per cent.; from 120° to 150°, to 0.5 per cent.; from 150° to 180°, to 1 per cent. The curve for  $Y_1^2 + Y_2^2$  is probably correct to 1 per cent. throughout the range.

These curves are drawn to different scales, as  $Z_1^2 + Z_2^2$  is approximately constant up to  $\theta = 120^\circ$ , while  $Y_1^2 + Y_2^2$  has oscillations of increasing amplitude. The curves for  $Y_1^2 + Y_2^2$  illustrate these oscillations up to the point where the last minimum occurs; after this the value of  $Y_1^2 + Y_2^2$  increases rapidly to a maximum at  $\theta = 180^\circ$ . The curves for  $Z_1^2 + Z_2^2$  illustrate the behaviour of this function up to  $\theta = 140^\circ$ , but do not show the last oscillation before the function begins to increase rapidly to its maximum at  $\theta = 180^\circ$ . For this range data are given in the tables.









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# PHILOSOPHICAL TRANSACTIONS

OF THE

# ROYAL SOCIETY OF LONDON.

SERIES A, Vol. 217. Pp. 315-360.



# BAKERIAN LECTURE.

# ON X-RAYS AND THE THEORY OF RADIATION.

 $\mathbf{BY}$ 

C. G. BARKLA, F.R.S.,

PROFESSOR OF NATURAL PHILOSOPHY IN THE UNIVERSITY OF EDINBURGH.

#### LONDON:

PUBLISHED BY THE ROYAL SOCIETY,

AND SOLD BY HARRISON AND SONS, ST. MARTIN'S LANE, W.C.,

Printers in Ordinary to His Majesty.

1917.

A 557.

# PUBLISHED BY THE ROYAL SOCIETY.

BURLINGTON HOUSE, LONDON.

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IX. Bakerian Lecture.—On X-rays and the Theory of Radiation.

By C. G. Barkla, F.R.S., Professor of Natural Philosophy in the University of Edinburgh.

Lecture delivered May 25, 1916,—MS. received January 3, 1917.

#### INTRODUCTION.

Of the various possible methods of approaching present day problems of electromagnetic radiation—particularly the problem of reconciling with the older electromagnetic theory those experimental facts which have led to the formulation of the Quantum Theory—the most profitable is probably to be found in the study of the phenomena of Röntgen radiation.

Primarily this is due not to the accuracy which may be attained in measurements upon radiation of this type, though this is an important factor, but to the fundamental nature of the phenomena themselves. The result of this is shown both in the simplicity and in the generality of the laws observed.

My purpose in this lecture is to call attention to some of the most significant experimental facts bearing on the nature of the processes resulting in the emission of X-rays—dwelling especially on the work I have been able to do in the last few years. Some of this I indicated in short notices appearing in 'Nature'\* at the beginning of last year, but the communications were too brief, perhaps, to be fully intelligible. Although the war has naturally retarded the work since then, certain facts have been established sufficiently conclusively, and, what is important, are sufficiently simple in themselves, to justify a further and more complete announcement. And though the theory put forward will provide subjects for investigation for some years to come, much might be lost by waiting for more complete evidence.

I therefore propose to give in outline the experimental basis for this theory. (A detailed description of the experiments themselves may be left for publication elsewhere.) In addition, the results of earlier work which has a direct bearing on recent problems of radiation will be incorporated. The significance of much of this work has probably been overlooked in discussions on the theory of radiation.

The known processes resulting in the emission of X-rays will be considered under

<sup>\* &</sup>quot;Problems of Radiation," 'Nature,' February 18, 1915, and "X-ray Fluorescence and the Quantum Theory," 'Nature,' March 4, 1915.

three heads, the names we apply to the radiations produced :—(1) scattered X-rays; (2) fluorescent (characteristic) `X-rays; (3) primary X-rays. This order has been chosen as probably leading to the greatest simplicity of treatment.

#### SCATTERED X-RADIATION.

When X-rays traverse matter of any kind, that matter becomes the source of a radiation of X-rays indistinguishable in kind from the primary radiation exciting it.\* What in many ways appears to be simply a re-directed or scattered primary beam is, however, more truly a new radiation. The similarity between the primary radiation and the secondary radiation of this type, while perhaps tending rather to mask the full importance of the phenomenon in reality enhances the value of the results obtained. The simplicity of necessity permits of less ambiguity in the interpretation of the experimental results.

The established facts which have an obvious bearing on the theory of radiation may be briefly stated.

- 1. Slight polarization of the primary radiation—as shown by the variation in intensity of radiation scattered around such a primary beam,†
- 2. Polarization of the scattered X-radiation, proceeding in a direction perpendicular to that of propagation of the primary radiation; (such as is shown in light scattered from the sky), and
- 3. The close agreement between wide limits, of the theoretical and experimental distribution of radiation scattered in a plane containing the direction of propagation of the primary beam,§

are inexplicable except on the transverse wave theory.

These experimental results were, in fact, looked for as necessarily following from such a theory. Similar results may, however, be obtained by transverse waves along strings or flexible tubes. An arrangement of flexible tubes may be used in lecture demonstrations illustrating mechanical phenomena exactly analogous to the three above-mentioned X-radiation phenomena.

- \* BARKLA, 'Phil. Mag.,' June, 1903; May, 1904; June, 1906; February, 1908.
- † BARKLA, 'Nature,' March 17, 1904; 'Phil. Trans. Roy. Soc,' vol. 204, 1905; 'Phil. Mag.,' June, 1906.
  - ‡ Barkla, 'Roy. Soc. Proc.,' A, vol. 77, 1906.
- § Barkla, 'Phil. Mag.,' February, 1908; Barkla and Ayres, 'Phil. Mag.,' February, 1911. When the secondary radiation experimented upon is purely scattered radiation, the distribution experimentally determined agrees with the theoretical distribution remarkably closely between the limits of 180° and about 30° for  $\theta$ . On the other hand the discrepancy between the two becomes very marked for small values of  $\theta$ , indicating either the necessity for some modification of the simple theory in this direction, or possibly the superposition of other effects. Various possibilities might be suggested, but they could not at present be regarded as more than speculations.

Difficult as the first two results would be to explain on any entity or quantum theory—that is, any theory assuming radiation itself to exist in definite indivisible bundles or quanta—perhaps the strongest evidence against this is provided by the third fact stated above. The distribution calculated and given by the expression  $I_{\theta} = I_{\pi/2} (1 + \cos^2 \theta)$  where  $I_{\theta}$  is the intensity of radiation scattered in a direction making an angle  $\theta$  with that of propagation of the primary beam depends essentially on a steady variation with direction, not of a number of indivisible entities, but of the energy density around a single radiating charge—an electron in this case.

4. Further, measurements of the energy of radiation scattered\* have furnished one of the most searching and critical of tests that could be applied to any theory.

In the early experiments it was found that the intensity of the radiation scattered from light elements was simply proportional to the mass of scattering substance traversed.† That is, the intensity of scattering per atom or molecule of scattering substance was proportional to its atomic or molecular weight—independent of density, chemical combination, or state of ionization of the substance. It thus became evident that neither atoms, molecules, nor gaseous ions were the scattering units, but that the scattering particles were the constituent electrons, and that in general, for light atoms, the number per atom was proportional to the atomic weight.

Using the result of a calculation given by Sir J. J. Thomson, for the fraction of a beam lost by scattering per centimetre of its path,

$$f = \frac{8\pi}{3} N \frac{e^4}{m^2} \mu^2$$
,

where N is the number per cubic centimetre of particles of charge e and mass m, it was calculated that the number of electrons per atom was several times the atomic weight. With the much more accurate data available for N,  $\frac{e}{m}$ , e, a few years ago I showed that the intensity is such as on the old spreading wave theory would be given by 1 electron per atom of H, 6 per atom of C, 7 per atom of N, 8 for O, 15 or 16 for S, &c.

These results concerning the constitution of the atom have been confirmed by independent evidence and are becoming generally accepted. Thus RUTHERFORD,  $\ddagger$  from experiments on the scattering of  $\alpha$  particles, arrived approximately at the complementary conclusion—that the central nucleus charge of an atom is  $\frac{we}{2}$  where w

<sup>\*</sup> Barkla, 'Phil. Mag.,' May, 1904; 'Jahrb. d. Radioaktivität u. Elektronik,' 1908; 'Phil. Mag.,' May, 1911.

<sup>†</sup> Hydrogen scattered about twice as much as the other elements, mass for mass. This at the time was thought to be due to impurity. CROWTHER, however, later obtained a value only slightly lower than this.

<sup>† &#</sup>x27;Phil. Mag.,' May, 1911.

is the atomic weight and e the electronic charge. (This nucleus, together with the number of electrons found from the scattering of X-rays, constitutes a neutral atom.)

Bohr\* on certain assumptions has shown that such an atom is capable of forming the basis of an explanation of the line spectra of hydrogen and helium, agreeing in a most remarkable way with experimental fact.

Moseley,† too, has given further evidence in support of the conclusion as to the number of electrons per atom. His "atomic numbers" are identical with the values given above.

This agreement is probably much more remarkable and significant than it at first sight appears. For apart from the orthodox electromagnetic theory of radiation, the intensity of the scattered radiation might have been anything between say 1000 part and 1000 times what was experimentally observed; yet the value experimentally determined twelve years ago—long before the precise significance of the results could be realized—agrees within a very small fraction with that to be expected on the modern conception of the atom and the old electromagnetic theory of radiation. Originally, while assuming this theory to hold, I used it to determine the number of electrons per atom. It is, however, perfectly legitimate now that the conclusions have been confirmed as indicated above, to use this agreement as evidence in support of this theory of radiation. The chances of such an agreement being accidental are almost infinitesimal.

Looking at the result in a somewhat different way, if for instance we imagined the gaseous ions to be the scattering units and calculated the number necessary in order to produce the scattering experimentally observed, we should find a number some millions of times the total number of molecules present in the scattering substance, that is, a number probably trillions of times too many. Yet applied to determine the number of electrons, the theory gives the number now accepted, certainly within a possible 5 to 10 per cent. error.

The theory on which this is based is the spreading wave theory. It assumes that the scattered radiation is the radiation resulting from the disturbance in electrons while under the influence of—in fact while controlled by‡—the primary radiation. Thus every electron in the matter traversed is influenced by every wave in the primary radiation passing over it, and receives a definite acceleration, f say, which is proportional to the electric intensity in the primary beam. The rate of radiation of energy from an electron with charge e and acceleration f is  $\frac{2}{3}\mu e^2 f^2/V$ —as first shown by Larmor. This summed up for all electrons gives the rate of emission of scattered radiation by those electrons; and this is readily expressed in terms of the rate of transmission of energy of primary radiation through the substance, for the acceleration

<sup>\* &#</sup>x27;Phil. Mag.,' November, 1913.

<sup>† &#</sup>x27;Phil. Mag.,' December, 1913.

<sup>‡</sup> At least the motion of the electrons resulting in radiation is not appreciably affected by atomic forces.

f is simply  $\frac{Xe}{m}$  where X is the electric intensity in the primary wave producing the disturbance. (See Sir J. J. Thomson's 'Conduction through Gases.')

Thus the theory assumes that radiation can take place from these electrons in any quantity whatever, and is not confined to units or quanta; that radiation is a continuous process not depending on any limiting or critical condition.

- 5. Again, in perfect agreement with this theory, I have found that the intensity of the radiation scattered from light elements varies little with the wave-length of the primary radiation. This indeed is also indicated by the above equation, the derivation of which was based on the assumption of independent action of the electrons.
- 6. And more recently\* it has been found that the intensity from the heavier atoms in which the constituent electrons are more closely packed, increases rapidly and continuously with the wave-length of the radiation unless this is very small. Such a result is to be expected on the wave theory when the wave-length becomes comparable with the size of the atom; ultimately a group of electrons and not an individual electron moves as a whole and becomes the scattering unit.† Further experimental results support this conclusion, and indicate that the radiation is emitted not in quanta but in any quantity, and that the process is a continuous process.

There is thus in the phenomena of scattering not only no suggestion of a quantum or entity in radiation, or of any discontinuity in the process of radiation involved, but there is some of the strongest positive evidence against any such theory. The tests which have been applied are the most searching and sensitive; the results appear conclusive. The phenomena observed become meaningless on any quantum or entity theory.

# Absorption.

As in the transmission of X-rays (particularly of short wave-length) through matter consisting of light elements only, the energy absorbed is practically all re-emitted as scattered X-radiation, the quantities radiated by each electron are identical with those absorbed. When there is little other absorption, viz., that associated with the emission of corpuscular and fluorescent X-radiation, the total absorption may be approximately calculated from the number of electrons in the matter traversed. It follows that this process of absorption is also a process which takes place in any quantity whatever, and is unlimited by any critical condition.

<sup>\*</sup> BARKLA and J. DUNLOP, 'Phil. Mag.,' March, 1916.

<sup>†</sup> When the group comprises all the electrons in the atom, the scattering per atom becomes on this theory proportional to the (atomic number)<sup>2</sup>, instead of to the atomic number, when the electrons scatter independently.

#### FLUORESCENT (CHARACTERISTIC) X-RADIATION.

Each element when traversed by X-rays emits X-radiations characteristic of the element;\* each characteristic radiation is unaffected by changes in the physical condition or state of chemical combination of the radiating element, and its quality is independent of that of the exciting primary radiation. But only primary radiations of shorter wave-length are able to excite the characteristic X-radiation (an extension of Stokes's law).†

All radiations hitherto definitely observed have fallen into two series—the K and L series.‡ (Experiments made within the last year, and briefly described in this paper, have established the existence of a third, a higher frequency series, which will be called the J series).§

The absorption method of analysing a radiation showed radiation of the K series from a particular element to be so homogeneous that it was regarded as giving a spectral line—the K spectral line; but the possibility of the L radiation consisting of more than one line was suggested by an obvious heterogeneity in the L radiation.

Interference experiments, however, have shown that both the K and the L radiations give spectra consisting of a number of neighbouring lines. In the greater portion of what follows these radiations of neighbouring wave-length will, however, be classed together as K or L radiations simply.

A characteristic radiation, unlike the scattered radiation, is uniformly distributed around a polarized primary beam and also in a plane containing the direction of propagation of primary radiation.

The intensity of a characteristic radiation\*\* varies in a definite regular way with a variation in the wave-length of the exciting primary beam, rising rapidly and afterwards falling more gradually as the wave-length of the primary diminishes.

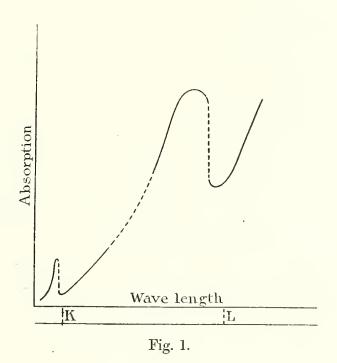
The uniformity in the distribution of the characteristic radiation around the radiating substance shows that in contrast with the process of emission of scattered radiation, the emission of a characteristic radiation is absolutely uncontrolled by the primary radiation exciting it. The phenomenon of emission is not an immediate

- \* BARKLA, 'Nature,' March 9, 1905; 'Phil. Trans. Roy. Soc.,' January, 1905; 'Roy. Soc. Proc.,' January, 1906; 'Nature,' February 15, 1906; 'Phil. Mag.,' June, 1906; 'Jahrb. der Radioaktivität u. Elektronik,' April, 1908. BARKLA and SADLER, 'Phil. Mag.,' September, 1907; 'Nature,' February 13, 1908.
  - † BARKLA, 'Jahr. der Rad. u. Elek.,' April, 1908; 'Proc. Phil. Soc. Camb.,' May, 1909.
- † Barkla, 'Proc. Phil. Soc. Camb.,' May, 1909; 'Phil. Mag.,' September, 1911; Barkla and Nicol, 'Nature,' August 4, 1910; 'Proc. Phys. Soc. Lond.,' December, 1911.
  - § An M series has recently been observed by Siegbahn and others.
- || Bragg, 'Roy. Soc. Proc.,' 1914; DE Broglie, 'Comptes Rendus,' 1914-16; Moseley, 'Phil. Mag., 1913-14; Siegbahn, 'Jahrbuch der Radioaktivität u. Elektronik,' 1916.
  - ¶ BARKLA, 'Phil. Mag.,' February, 1908; BARKLA and AYRES, 'Phil. Mag.,' February, 1911.
  - \*\* BARKLA and SADLER, 'Phil. Mag.,' May, 1909.

result of the passage of the primary beam, but arises only indirectly from it; the process is dependent on some critical condition, as evidenced by Stokes's law. Here at once we see the possibility of the applicability of some kind of quantum theory.

The most significant evidence as to the origin of the characteristic radiation comes from a study of the accompanying phenomena of (1) absorption of the exciting primary radiation; and (2) emission of electrons by the radiating substance, in the form of a corpuscular radiation. It is necessary here to introduce a brief account of these phenomena.

Absorption.—The absorption of a primary radiation is due to various causes which can be quite readily distinguished;\* they are distinct and apparently independent absorptions. Thus the total absorption in a particular element of radiations of various wave-lengths may be represented by a curve of the form shown in fig. 1, the ordinates



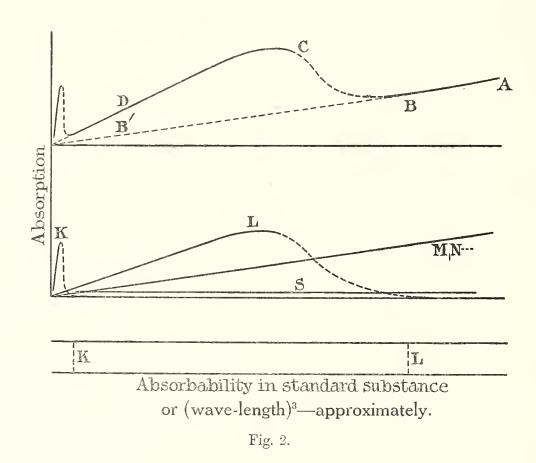
in which indicate the absorptions of radiations whose wave-lengths are given by the abscissæ. The curve is of simpler form however, if instead of wave-lengths we plot as abscissæ the absorbabilities in some standard substance which has no spectral lines in the part of the spectrum considered.† Then the absorption curve takes the form of fig. 2. This, however, for the sake of clearness is not drawn to scale. The lower portion of the figure gives the spectral lines of the substance traversed.‡ Proceeding

<sup>\*</sup> Barkla and Sadler, 'Phil. Mag.,' May, 1909; Barkla and Coller, 'Phil. Mag.,' June, 1912; Barkla, 'Proc. Phil. Soc. Camb.,' May, 1909; Barkla and Sadler, 'Nature,' July 16, 1908, and March 11, 1909.

<sup>†</sup> Or the (wave-length)<sup>3</sup> approximately, as Hull and Rice have shown.

<sup>‡</sup> These curves do not show the exact relation in the regions of very rapid change, as the radiations used were not perfectly homogeneous.

from right to left, i.e., from long to short waves, we see that sudden increases in absorption occur when the primary radiation becomes of shorter wave-length than the radiations characteristic of the absorbing substance—that is, when the characteristic radiations begin to be excited in the absorbing substance—and that the absorption afterwards gradually approaches proportionality with the absorption in the standard substance—as shown by the approximation to a straight line through the origin. Thus the line ABB' shows what would be the absorption of radiations of various wave-lengths if there were no L characteristic radiation excited in the absorbing substance. The rise as shown by the portion BCD is associated with the emission by the absorbing substance of the fluorescent X-radiation of series L. The difference



between the ordinates of the curve BCD and BB' gives the absorption associated with the emission of L radiation, or what we shall call the "L" absorption ( $E_L$ ). In a similar fashion we can get the "K" absorption  $E_K$ . The lower portion of fig. 2 indicates the various independent absorptions S,  $E_K$ ,  $E_L$ ,  $E_{M,N...}$  in separate curves where S = energy absorbed and re-emitted as scattered radiation,  $E_K$ ,  $E_L$ ,  $E_{M,N...} =$  energy absorbed in association with the emission of characteristic radiations of series K, L, and M, N, ... respectively. The absorption S due to the process of scattering is approximately independent of wave-length, so is represented by a horizontal line. It however rises considerably at the long wave-length end if the wave-length be sufficiently great.

Thus the total absorption E may be written

$$E = S + E_J + E_K + E_L + \dots$$

in which all the right-hand terms appear to be independent quantities.

Corpuscular Electronic Radiation.—In addition it may be shown that the corpuscular radiation (i.e. the radiation consisting of high speed electrons emitted from substances exposed to X-rays) may be divided into several distinct groups, each associated with the emission of a fluorescent X-radiation of a particular series; thus the total corpuscular radiation  $C = C_J + C_K + C_L + \dots$  where  $C_J$ ,  $C_K$ ,  $C_L$ , are corpuscular radiations definitely associated with the emission of J, K, and L characteristic radiations respectively. This we shall proceed to show.

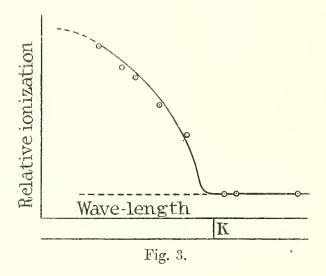
C. T. R. Wilson's condensation experiments\* show that X-ray ionization is due to the corpuscular radiation which the X-rays excite in the gaseous substance ionized. (All other investigations of less direct nature which at first appeared to indicate this only to a partial extent may now be shown to confirm this conclusion as accurately as the possible errors of experiment allow.) Wilson's experiments indicate, too, that there is little or no variation in the velocity of the electrons ejected by X-radiation of one wave-length. For the length of path of an electron was shown by Whiddington to vary as the fourth power of the velocity; consequently an electron with half the maximum velocity of ejection would have a path only one-sixteenth that of the other. If then the velocities of ejection ranged from zero to the maximum, Wilson's experiments would show a very large number of short paths. Simple observation of the photographs showing the trails of the ejected electrons is sufficient to convince one that little variation of initial velocity exists, and that such variation as is observable in the lengths of the trails is probably due either to the heterogeneity of the primary beam, or to fore-shortening of the trails. Ionization of air by homogeneous X-rays is therefore through the agency of electrons emitted with one velocity, approximately, if not accurately.

From experiments on ionization it may readily be shown that the corpuscular radiation consists of several independent groups each associated with the emission of a particular fluorescent X-radiation. For the ionization of a substance by X-rays of varying wave-length varies with the wave-length of these rays in a manner similar to that of the absorption. Thus the ionization in a substance R say, is proportional to the ionization in a second substance for a range of wave-lengths not near to a spectral line of either on its shorter wave-length side. As the wave-length of the primary X-radiation is diminished beyond that of a spectral line of R, there is a sudden rise in the ratio of ionizations, and the ratio gradually approaches a constant

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' 1912.

<sup>†</sup> This refers to the investigations of BARKLA, BRAGG, BEATTY, BARKLA and PHILPOT. BRAGG was the first to insist that ionization was entirely due to the high speed corpuscles.

but higher value until another series of spectral lines in one of the substances is passed when a further change occurs. This is shown in fig. 3, in which the upper portion shows the ratio of ionizations plotted against wave-length of the X-rays used. In the figure the horizontal broken line indicates the relation that would have existed if there had been no radiation characteristic of R within the range of wave-lengths used, and no corresponding increase in the corpuscular radiation from the substance R. The rise of the curve above the broken line gives the increase in ionization associated with the emission of the fluorescent X-radiation of series K, say. As ionization is due to the emission of high speed electrons by the substance, the difference between the two curves is due to additional electrons emitted in association with the fluorescent characteristic X-radiation of series K. We thus see and are able to measure accurately the effect of what will be called the K corpuscular radiation, to distinguish it from the L, M, N corpuscular radiations which are emitted in association with the similarly named fluorescent (characteristic) X-radiations.



As it has recently been shown\* that there is no appreciable difference between the velocities of these electrons of different groups K, L, &c., it follows that ionization experiments give us accurate data for determining the relative numbers of electrons in the various groups emitted by a substance when exposed to X-rays. This method has been used in some preliminary determinations which are described later.

ENERGY RELATIONS BETWEEN THE CORPUSCULAR AND THE FLUORESCENT RADIATIONS, AND THE EXCITING PRIMARY RADIATIONS.

In investigating the process of emission of the characteristic X-radiation when this is excited by another shorter wave-length radiation, a study of the relation between the energies of primary radiation absorbed and the associated corpuscular and fluorescent radiations emitted, is of fundamental importance. It is, however, necessary first

<sup>\*</sup> BARKLA and SHEARER, 'Phil. Mag.,' December, 1915.

of all to analyse the absorption of the primary radiation into J, K, L, M, ... and S absorptions, the secondary corpuscular radiation into J, K, L, M corpuscular radiations, and the secondary X-radiations into J, K, L, M ... and S radiations, and observe only the relations between the corresponding quantities, or at any rate to do this for one particular series, say the K series, with primary radiations of various wave-lengths.

# Energy of Fluorescent (Characteristic X-radiation).

The energy of the fluorescent X-radiation was first measured and expressed in terms of the energy of the absorbed primary X-radiation by Barkla and Sadler.\* In this as in all similar measurements the energies of radiations of different wavelengths were compared by their total ionizing powers. With a primary radiation of wave-length considerably shorter than that of copper K radiation, the energy of the X-radiation emitted was about 33 per cent. of the energy absorbed, or about 40 per cent. of the K absorption; with a primary of shortening wave-length the fraction diminished.† For other substances the transformation fraction was of the same order of magnitude.

Sadler, tworking with approximately homogeneous primary radiations, made a much more systematic and accurate investigation of the energy in the fluorescent characteristic radiations from several substances, and expressed this in terms of the primary energy absorption obtained by Barkla and Sadler. The results obtained are given in Tables I. and II. Table I. shows the fraction of the total energy absorbed

Table I.—Giving Fraction  $(F_{\kappa}/E)$  of Total Primary Energy Absorbed transformed into Fluorescent X-radiation of Series K.

Drimony radiation	Wave-length	Substance exposed to primary radiation.					
Primary radiation.	$(\alpha_1)$ .	Cr.	Fe.	Co.	Ni.	Cu.	Zn.
Fe X-radiation (series K) Co ,, ( ,, ) Ni ,, ( ,, ) Cu ,, ( ,, ) Zn ,, ( ,, ) As ,, ( ,, ) Se ,, ( ,, ) Ag ,, ( ,, )	cm. $1 \cdot 93 \times 10^{-8} \\ 1 \cdot 78 \times 10^{-8} \\ 1 \cdot 65 \times 10^{-8} \\ 1 \cdot 54 \times 10^{-8} \\ 1 \cdot 43 \times 10^{-8} \\ 1 \cdot 17 \times 10^{-8} \\ 1 \cdot 10 \times 10^{-8} \\ 0 \cdot 56 \times 10^{-8}$	0.151 $0.132$ $0.125$ $0.110$ $0.095$ $0.067$ $0.055$	$\begin{array}{c} (0 \cdot 098) \\ 0 \cdot 216 \\ 0 \cdot 194 \\ 0 \cdot 179 \\ 0 \cdot 132 \\ 0 \cdot 106 \\ 0 \cdot 058 \end{array}$	0·066 0·262 0·243 0·170 0·130	0.080 0.289 0.203 0.163	0.086 $0.248$ $0.199$ $(0.105)$	0·281 0·239 (0·113)

<sup>\* &#</sup>x27;Phil. Mag.,' October, 1908.

<sup>†</sup> At the same rate as the fraction absorption in air absorption in Cu. The range of wave-lengths, however, was short.

<sup>† &#</sup>x27;Phil. Mag.,' July, 1909.

which was transformed into K fluorescent (characteristic) radiation; Table II. the fraction of energy of K absorption which re-appeared as K fluorescent radiation. Before generalising from these results, we must eliminate all those which are obviously unreliable. Thus when the primary radiation was of just shorter wave-length than

Table II.—Giving Fraction  $(F_K/E_K)$  of Primary Energy Specially Absorbed—" K Absorption"—transformed into Fluorescent X-radiation of Series K.

Primary radiation	Wave-length	Substance exposed to primary radiation.					
Primary radiation. $(\alpha_1)$ .		Cr.	Fe.	Co.	Ni.	Cu.	Zn.
Fe X-radiation (series K) Co ,, ( ,, ) Ni ,, ( ,, ) Cu ,, ( ,, ) Zn ,, ( ,, ) As ,,* ( ,, ) Se ,, ( ,, ) Ag ,, ( ,, )	cm. $1 \cdot 93 \times 10^{-8}$ $1 \cdot 78 \times 10^{-8}$ $1 \cdot 65 \times 10^{-8}$ $1 \cdot 54 \times 10^{-8}$ $1 \cdot 43 \times 10^{-8}$ $1 \cdot 17 \times 10^{-8}$ $1 \cdot 10 \times 10^{-8}$ $0 \cdot 56 \times 10^{-8}$	0.176 $0.154$ $0.145$ $0.127$ $0.109$ $0.0757$ $0.0624$	(0.504)? 0.252 0.225 0.207 0.150 0.120 0.062	0.287 ? $0.305$ $0.282$ $0.195$ $0.149$	0·288? 0·340 0·233 0·187	$0.358 ? \\ 0.288 \\ 0.231 \\ (0.118)$	$0.327 \\ 0.278 \\ (0.132)$

the fluorescent radiation which it was exciting, the latter appeared in only small intensity accounting for from 2 to 10 per cent. of the total absorption (Table I.). Owing to this and to the admixture of scattered radiation, the possible percentage error was extremely high; these results expressed in terms of the special K absorption, which also being a difference effect is difficult to measure with any accuracy in this region, are seen to be irregular and of no value. We must therefore reject these.\*

By plotting the fraction  $\frac{K \text{ fluorescent radiation (energy)}}{K \text{ primary absorption (energy)}}$  against wave-length of the primary radiation it is seen that the other results are perfectly regular (fig. 4). Of the energy of primary radiation absorbed in association with the emission of K radiation, the greatest fraction is transformed into K fluorescent radiation when the wave-length of the primary radiation differs least from that of the fluorescent radiation. As the wave-length of the primary radiation diminishes the fraction so

<sup>\*</sup> A note of interrogation indicates these in Table II. Reference to the corresponding values in Table I. shows them to be based on the experimental determination of small quantities. Their irregularity, where all else is regular, is evidence of their unreliability except as indicating orders of magnitude: the reason is obvious. If these values could be experimentally determined with accuracy, they would probably be quite different from those obtained by the use of a perfectly homogeneous radiation of wavelength given in column II. Still, this fact would not appreciably affect the conclusions drawn below, because the values are compared with corresponding absorptions—that is, with the absorptions of identical radiations.

transformed diminishes also, the relation being almost a linear one within the range of these experiments.

[Originally the writer determined the wave-length of a primary radiation from the speed of the electrons it ejects, *i.e.*, from the equation  $\frac{1}{2}mv^2 = hn$ , where h is Planck's constants, -v being obtained from Whiddington's law. These results are plotted in fig. 4A as they are somewhat more regular than those in fig. 4.]

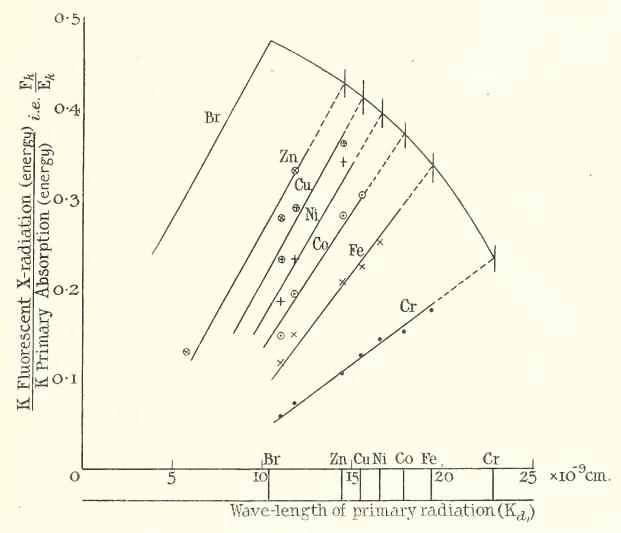
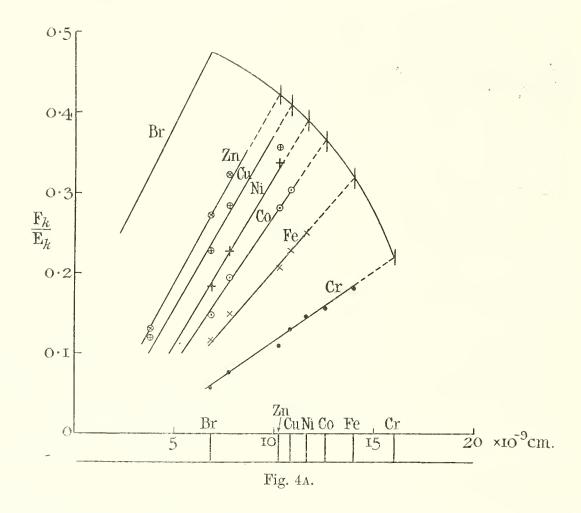


Fig. 4. Showing the fraction of the energy of primary radiation absorbed—K absorption—which is transformed into fluorescent (characteristic) X-radiation of series K, in elements Cr, Fe, Co, Ni, Cu, Zn.

It will be noticed that by producing these lines backward so as to get the transformation fraction when the primary has a wave-length just shorter than the fluorescent (characteristic) radiation, this fraction approaches 0.5 for the heavier elements; there is evidence, too, that from the heaviest substances the maximum transformation coefficient does not exceed about 0.5. This is seen by plotting the maximum transformation coefficient for various elements against their atomic weight or by continuing the curve in fig. 4 to the left; the value found by extrapolation is evidently very near to 0.5.

In arriving at these results the energies of primary and fluorescent radiations have been compared by their total ionizing powers. Now the only possible error arising from this assumption occurs when primary and fluorescent radiations differ considerably in wave-length; when the primary is of just shorter wave-length than the characteristic radiation, the error becomes vanishingly small, consequently cannot affect the accuracy of the determination of the maximum transformation coefficients. As will be seen later, there is also strong evidence that even when the primary and fluorescent radiations are widely different in wave-length, the error is certainly not large, if it is of appreciable magnitude.

The substances Cr, Fe, Ni, Co, Cu, Zn in which the transformation coefficients have been determined are not suitable for accurate experimental determination of the energy of the *corpuscular* radiation—nor if they were, would they be the most



suitable for the purpose of the present investigation. There is, however, little or no disadvantage in obtaining the transformation coefficients in the substance bromine by extrapolation from the above results, for the results experimentally obtained with elements of lower atomic weight are so regular as to leave little room for error in the results so determined.

The advantages in the choice of bromine as the experimental substance are (1) it can be obtained in the gaseous state alone or in combination with light elements, so that ionizations may readily be obtained and the energy of corpuscular radiation accurately measured; (2) its K spectral lines are of about the most suitable wave-length for

observation of the energy transformations of an exciting primary radiation through a long range of wave-lengths; (3) the energy of fluorescent radiation from bromine is not far removed from the limiting value observed; the behaviour of bromine is thus probably typical of the greatest number of elements, and for this reason the experimental results are the least open to question.

The relation between  $\frac{\text{K fluorescent radiation (energy)}}{\text{K primary absorption (energy)}}$  and wave-length of primary radiation, when bromine is the fluorescent substance, is given in fig. 4, along with the position of the bromine spectral lines of series K, and is reproduced on a different scale in fig. 5, curve F. The continuous portion of the curve we may thus regard as obtained by direct experiment. It should be pointed out that the wave-length of the  $K_{\alpha_1}$  line has been adopted throughout.

There is much evidence, too, that the curve must turn through the origin as indicated by the broken line (fig. 5). This represents a small, decreasing, and ultimately vanishing amount of fluorescent X-radiation emitted by a substance exposed to a primary radiation of small and decreasing wave-length.

- Thus (1) Barkla and Philpot\* showed that when a primary radiation is of much shorter wave-length than any characteristic radiation it excites, its absorption results in the emission of approximately the same number of electrons, whatever the absorbing substance; it follows from the complementary property of the characteristic (fluorescent) X-radiation† that there cannot be varying amounts of fluorescent radiation unless this is so weak that variations would not be observable. This means that all the curves must pass through the same point; the only point through which all the lines in fig. 4 can turn consistently with the experimentally observed results is the origin, or a point near to it.
- (2) There is little doubt that air like other substances emits a K radiation which is of very long wave-length compared with an ordinary primary beam of X-rays; yet C. T. R. Wilson's cloud experiments show few, if any, very short tracks such as would be produced by the re-absorption of such a radiation if emitted in appreciable intensity. We conclude that with a primary radiation of comparatively short wavelength, the fraction of energy transformed into fluorescent X-radiation becomes very small.
- (3) Again, in the most accurate measurements by Beatty and by Bragg of the corpuscular radiation from metal sheets, the possibility of the existence of such soft fluorescent radiations in any large quantity has been entirely neglected; yet the results show sufficient consistency to indicate that the characteristic radiations of longer wave-length must account for only a small portion of the energy of primary radiation absorbed.

<sup>\* &#</sup>x27;Phil. Mag.,' June, 1913.

<sup>†</sup> See p. 336.

(4) Support for the general conclusion given above can also be obtained from some results incidentally got by Bragg and Porter.\* I have used these experimental results to determine the fractions as given in Table II., with the results given below:—

D.:	$\mathrm{F}_{\scriptscriptstyle\mathrm{K}}/\mathrm{E}_{\scriptscriptstyle\mathrm{K}}.$					
Primary radiation.	Fe.	Ni.	Cu.	Zn.		
Zn X-rays	$0.236 \\ 0.227 \\ 0.17$	$0.322 \\ 0.336 \\ 0.29$	0.394 $0.34$	$0.432 \\ 0.39$		

All these values are a little higher than SADLER's and indicate a smaller change with the wave-length of the primary radiation, that is, a smaller slope in the curves of fig. 4;† but the important features to be observed in the results of Table II. are in evidence here. They are so consistent, especially in the case of the radiators of higher atomic weight, that little error in these seems possible.

Briefly and approximately the results of experiments on the heavier elements are these:—When the wave-length  $(\mu)$  of the primary radiation is just less than that  $(\mu_{K})$  of the fluorescent (characteristic) radiation, of the energy specially absorbed in association with the emission of the fluorescent radiation, nearly 0.5 is re-emitted as fluorescent radiation. As  $\mu$  becomes less, the fraction diminishes almost proportionately, until for a primary radiation of very small wave-length, the energy of the fluorescent radiation becomes a very small fraction of the energy of the primary radiation  $(E_{K})$  specially absorbed.

# Energy of Corpuscular (Electronic) Radiation.

Though measurements of the energy of the corpuscular radiation emitted by substances exposed to X-rays have been made by a number of investigators, the changes taking place as the wave-length of the exciting radiation passes from one side of a spectral line to the other have not been studied. In addition the results obtained by different investigators have been by no means consistent. It seemed probable that much more reliable results could be obtained by experimenting on substances in the gaseous state, and estimating the energy of corpuscular radiation by the ionization it produced on complete absorption in the gas itself. The method

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' May, 1911.

<sup>†</sup> These results from experiments with lighter elements agree more closely with theory than do those of Sadler.

can be most clearly explained by reference to the results obtained in one particular substance, ethyl bromide.

Experiments were commenced by the writer and Mr. M. Thomas\* on the ionization produced in ethyl bromide vapour by a number of approximately homogeneous X-radiations of various wave-lengths. One series of these experiments was made in a very large ionization chamber cylindrical in shape, of length 68 cm., diameter 44 cm., and with an axial electrode connected through a side tube to an external electroscope. Ionization-pressure curves were obtained in the usual way and with great care, both with air and with ethyl bromide in the chamber, all other conditions being similar. After the usual correction for absorption in the gases themselves, the relative ionizations given in Table III. were obtained. Column I.

TABLE III.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Source of X-rays.	Approximate wave-length $(K_{\alpha_1})$ ,	Absorbability $\left(\frac{\lambda}{\rho}\right)_{\mathrm{Al.}}$	Ionization coefficient in $C_2H_5Br$ Ionization coefficient in air $(K, L \dots)$ .	"K" ionization coefficient in $C_2H_5B_r$ Ionization coefficient in air (K, L)	Absorption in $C_2H_5B_r$ Absorption in air (K, L, M, &c.)	"K" absorption in $C_2H_5B_r$ Absorption in air (K, L, M, &c.)	Ionization in C <sub>2</sub> H <sub>6</sub> Br (L, M, N, &c.) Ionization in air (K, L, M, &c.) for equal absorptions of primary radiation.	Ionization in C <sub>2</sub> H <sub>5</sub> Br (K)  Ionization in air (K, L, M, &c.)  for equal absorptions of primary radiation.
Cu As Se	cm. $1 \cdot 54 \times 10^{-8}$ $1 \cdot 17 \times 10^{-8}$ $1 \cdot 10 \times 10^{-8}$	47.7 $22.5$ $18.9$	50 49·3 50·5		$24 \cdot 4$ $25 \cdot 3$ $26 \cdot 2$		2·05 1·94 1·93	
Sr Mo Ag Sn Ce	$0.871 \times 10^{-8}  0.710 \times 10^{-8}  0.562 \times 10^{-8}  0.487 \times 10^{-8}  0.355 \times 10^{-8}$	$9 \cdot 40$ $4 \cdot 70$ $2 \cdot 50$ $1 \cdot 57$ $0 \cdot 6$	$ \begin{array}{c} 165 \\ 221 \\ 279 \\ 298 \times 1 \cdot 32 \\ = (393) \\ 342 \times 1 \cdot 39 \\ = (475) \end{array} $	115 171 229 343 425	159 190 210 267 321	133 164 184 241 295		0 · 865 1 · 04 1 · 255 1 · 42

<sup>\*</sup> Shortly after the outbreak of war, Mr. Thomas was given a commission in the army, so was unable to complete the work he commenced so successfully. He was killed in action on December 31, 1915.

gives the source of the homogeneous rays used to ionize the gases; column II. the approximate wave-length of the radiation; column III. the mass coefficient of absorption of the radiation in aluminium; column IV. the ratio of ionization coefficients in ethyl bromide and in air. Thus when two similar beams of radiation traverse two equally thin layers of ethyl bromide and air at the same pressure and temperature, and in each case the gas absorbs its own corpuscular radiation completely, and all fluorescent radiations of no greater penetrating power than this corpuscular radiation, the ionization in ethyl bromide varies from 50 to about 342 times that in air as the wave-length of the radiation diminishes, or from 50 to 475 times that in air by K, L, M... corpuscles (electrons) alone, as we shall see later. Of course the ratio of the absorption in ethyl bromide to that in air is also high, and it varies with the wave-length of the radiation used. It should be pointed out, however, that the K characteristic radiation from bromine when excited was allowed to escape without adding its effect to the total ionization measured in ethyl bromide.

Thus when Cu, As and Se "K" radiations were used as ionizing agents, the ionization in ethyl bromide (produced by L, M, N electrons) was about 50 times that in air. But when Sr, Mo, Ag, &c., radiations were used, the "K" corpuscular radiation was emitted by the bromine in ethyl bromide and produced an increase in the relative ionization. Subtracting 50 from the values in column IV. we get the effect of the additional (K) electrons, *i.e.*,

ionization in 
$$C_2H_5Br$$
 due to K electrons alone ionization in air by K, L... electrons

as given in column V. Column VI. gives the relative absorptions of the ionizing radiations in ethyl bromide and air at the same pressure and temperature. Here again there is a large increase when the particular radiation is of sufficiently high frequency to excite the K radiation in bromine. Subtracting the ratio obtained when no K fluorescent radiation was excited from that obtained when it was excited, we get the values in column VII. which consequently represent the

$$\frac{\text{K absorption in } C_2H_5Br}{\text{absorption in air } (K,\,L,\,M,\,\ldots)}.$$

Dividing values in column IV. by the corresponding values in column VI. we get

$$\frac{\text{ionization in } C_2H_5Br}{\text{absorption in } C_2H_5Br} \cdot \frac{\text{ionization in air } (K, L, ...)}{\text{absorption in air } (K, L, ...)},$$

which is

# ionization in C<sub>2</sub>H<sub>5</sub>Br ionization in air (K, L, ...)

for equal absorptions of the ionizing radiations (column VIII.).

Similarly dividing the values in column V. by the corresponding values in column VII. we get ionization in C<sub>2</sub>H<sub>5</sub>Br due to K electrons for equal absorptions

of the ionizing radiations (see column IX.).

Thus column VIII. gives ionization in ethyl bromide due to L, M, N, &c., electrons, relative to ionization in air due to K, L, M, N, &c., electrons, produced by equal absorptions in the two gases. Column IX. gives ionization in ethyl bromide due to K electrons alone, relative to ionization in air due to K, L, M, N, &c., electrons, for equal absorptions of the ionizing radiation in the two gases. As ionization produced in a given gas by a given homogeneous X-radiation is proportional to the number of electrons in the corpuscular radiation producing that ionization, we see from columns VIII. and IX. that when the exciting primary radiation is of just shorter wave-length than the bromine K radiation, the K absorption is accompanied by the emission of a much smaller number of electrons than is the L, M, N absorption. For instead of 205, 194, 193, L, M, and N electrons, there are emitted 87, 104, 125, 142, 144, K electrons for primary radiations of higher frequency; or for equal absorptions of energy there are only about half as many K electrons emitted as L, M, ... electrons, when the primary radiation is of just shorter wave-length than the K characteristic radiation. As primary radiations of shorter and shorter wave-length are used, the number of K electrons emitted more closely approaches the number of L, M, ... electrons emitted for an equal absorption of energy of primary radiation. At first sight it appears from column VIII. as though twice as many electrons are emitted from C<sub>2</sub>H<sub>5</sub>Br as from air when equal absorptions of Cu, As and Se radiations take place. This, however, is due to the fact that more ions are produced by a high speed electron moving through C<sub>2</sub>H<sub>5</sub>Br than through air. The former is more easily ionized. The factor by which the numbers 2.05, 1.94, 1.93, &c., in columns VIII. and IX. must be divided to give the relative numbers of electrons emitted by C<sub>2</sub>H<sub>5</sub>Br and air is approximately 1.75.\* Thus number of L, M, N, ... electrons emitted by Br number of K, L, M, ... electrons emitted by air

and number of K electrons emitted by Br number of K, L, M, ... electrons emitted by air for equal absorptions of energy are given in Table IV., columns II. and III., for primary radiations of wave-length indicated in column I.

<sup>\*</sup> The value given by Barkla and Philpot ('Phil. Mag.,'June, 1913) as a first approximation was 1.6. This, however, needed a small correction, the magnitude of which was unknown at the time, but has since been found from experiments by Carse to raise the value to about 1.75. The correction was necessary on account of the appreciable reflexion or return through the face of incidence of corpuscles on entering the substance ethyl bromide.

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Approximate wave-length of primary radiation.	Number of L, M, electrons emitted by Br Number of K, L, M, electrons emitted by air for equal absorptions of primary radiation.	Number of K electrons from Br Number of K, L, M, electrons from air for equal absorptions of primary energy.
cm. 1·54 × 10 <sup>-8</sup> 1·17 × 10 <sup>-8</sup> 1·10 × 10 <sup>-8</sup>	$1 \cdot 17$ $1 \cdot 11$ $1 \cdot 10$	
$\begin{array}{c} 0.87 \times 10^{-8} \\ 0.71 \times 10^{-8} \\ 0.56 \times 10^{-8} \\ 0.49 \times 10^{-8} \\ 0.355 \times 10^{-8} \end{array}$		0.49 $0.59$ $0.72$ $0.81$ $0.82$

This shows the numbers of electrons emitted by ethyl bromide and by air to be about equal when the primary radiation is of longer wave-length than that characteristic of bromine ( $K_{a_1} = 1.035 \times 10^{-8}$  cm.).\*

# First Approximation.

The significance of these results is most easily understood if at first we express them approximately.

Let the wave-length of the primary radiation be  $\mu$ , and that of the K fluorescent (characteristic) radiation of the substance bromine be  $\mu_{K}$ . Then when  $\mu$  is greater than  $\mu_{K}$ , for a given absorption of the primary radiation, the same number of electrons is emitted by ethyl bromide (L, M, N, &c., electrons) as by air (K, L, M, N, &c., electrons), as shown in Table IV., column II.

When  $\mu$  is just less than  $\mu_K$ , the additional (K) absorption in ethyl bromide is accompanied by the emission of only half as many electrons—that is, only half the K energy absorbed is re-emitted as energy of K corpuscular radiation (column III.).†

- \* It might be suggested that the sudden decrease in ionization is possibly due to a sudden decrease not of the number of electrons emitted, but of the total ionizing power of each electron when its velocity is increased beyond a critical value—that necessary to excite the K fluorescent radiation. There is, however, plenty of evidence against this—(a) theoretically it is highly improbable; (b) such changes in relative ionizing power with velocity have not been observed; and conclusively (c) the decrease above described in this case is true when the electrons are absorbed not in the substance itself, but in another gas (see p. 336).
- † We here assume that the energy of an X-radiation is approximately equal to that of the full corpuscular radiation which it excites in a substance completely absorbing it, when the conditions are such that little energy is re-emitted in the form of either scattered or fluorescent (characteristic) X-radiation. The evidence for this is very weighty and may be summarized as follows:—

When during the transmission of a primary radiation through matter there is very little transformation into corpuscular radiation, practically the whole of the loss of energy is accounted for by the process of

But as  $\mu$  becomes smaller, an increasing fraction of the energy absorbed (K absorption) goes into the K corpuscular radiation. And the rate of change indicates that with a primary radiation of very small wave-length, practically the whole of the K absorption would be accounted for by the K corpuscular radiation alone. There is, in addition, very strong indirect evidence that when  $\mu$  is very small, nearly all the energy absorbed is re-emitted as corpuscular radiation, for, as already pointed out, whatever the absorbing substance under these conditions, the energy of this corpuscular radiation is approximately a constant.

Similar measurements have been made of the energy of corpuscular radiation emitted from iodine from observations of the ionization in methyl iodide. Owing to complications—the causes of which need not be discussed—difficulty was found in determining accurate values by extrapolation, and such as were obtained only indicated the energy of corpuscular radiation when the wave-length of the primary radiation was slightly less than that of the K fluorescent radiation. They show that when the K radiation from barium ( $\mu_{K\alpha} = 0.39 \times 10^{-8}$  cm.) is incident on iodine ( $\mu_{K\alpha} = 0.44 \times 10^{-8}$  cm.) nearly 0.5 of the K absorption is accounted for by the K corpuscular radiation from iodine. This is in as close agreement with the corresponding value for bromine given above as could be expected.

scattering, showing there is little energy truly absorbed except as the accompaniment of the emission of corpuseular radiation.

When absorption is accompanied by the emission of only very little fluorescent (characteristic) X-radiation and a negligible amount of scattered radiation, the number of high speed electrons emitted by the absorbing substance is approximately independent of the substance; so for a radiation of a particular frequency absorbed, the number of high speed electrons emitted is proportional to the energy absorbed.

Even when a considerable amount of fluorescent radiation is emitted—about half of the total energy absorbed—the number of high speed electrons emitted by certain substances is still approximately proportional to the energy absorbed minus that re-emitted as fluorescent radiation. Thus, in many cases, energy of high speed electrons emitted by an absorbing substance = k (E - S - F) where k is a constant, E is energy of primary radiation absorbed, E the amount of energy scattered, and E the amount re-emitted as fluorescent radiation.

This has been shown to be true (approximately) in  $C_2H_5Br$  when S is small and  $F = \frac{1}{2}E$ . And if we assume that the energy of X-radiations differing in wave-length may be measured by their total ionizing power in a given gas, it is true in  $C_2H_5Br$  as the wave-length of the primary diminishes and the proportions of fluorescent and corpuscular radiations change.

This is strong evidence both that the equation holds in ethyl bromide while the wave-length of the primary radiation changes considerably, and at the same time that the energy of X-radiation of various wave-lengths may be compared at least approximately by their ionizing powers.

As the equation holds under such a variety of conditions, and through various transformations, we conclude that under these conditions the energy of the corpuscular radiation is not only proportional to, but equals that of the energy of X-rays disappearing, or that k = 1. (Under other conditions, probably in lighter elements, there appears to be appreciably less corpuscular radiation than would be expected from this relation. The energy disappearing may not be re-emitted in radiation of any recognisable form.)

As the energy of a corpuscle, too, has been found to be approximately that of a quantum of radiation measured by other methods, we conclude that in the cases given above the number of quanta of X-radiation absorbed, when not re-emitted as X-radiation, is measured by the number of high speed corpuscles emitted.

Again, in the light of the results obtained from these experiments on bromine, the results of experiments on corpuscular radiation from metal plates by Beatty and Brage, though somewhat irregular and decidedly fragmentary for the purpose of this investigation, may be seen to point to the generality of the above laws—at least in general features if not in detail.

Further experiments on the corpuscular radiation from substances in the form of plates indicate, though with a greater possible error, that when  $\mu$  is slightly less than  $\mu_{K}$  the K corpuscular radiation accounts for about 0.4 of the K absorption. Such measurements can however, be regarded as giving only the order of magnitude of these quantities.

Thus direct and indirect experiments indicate that when the wave-length of the primary radiation  $\mu$  is just less than that  $(\mu_K)$  of a fluorescent radiation, of the energy specially absorbed in association with the K fluorescent radiation, nearly 0.5 is re-emitted as energy of corpuscular radiation. As  $\mu$  becomes less, the fraction increases, until for primary radiation of very small wave-length, nearly all the energy absorbed (K absorption) is re-emitted as K corpuscular radiation. The values actually obtained for the K energy emitted by ethyl bromide as K corpuscular radiation are plotted in fig. 5, Curve C, for various wave-lengths shown by the abscissæ.

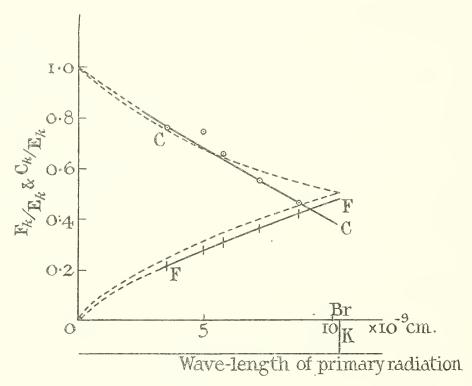


Fig. 5. Showing fraction of energy of primary beam absorbed—K absorption—transformed into K fluorescent (characteristic) radiation, and into K corpuscular radiation (lines FF and CC respectively).

It is evident at once that the energy of K corpuscular radiation from bromine is approximately complementary to that of the K fluorescent X-radiation. A full discussion is, however, given later.

#### THEORY OF FLUORESCENT X-RADIATION.

The conditions essential to the emission of a fluorescent X-radiation show that it originates in some exceptional disturbance of an atomic system. In the phenomena considered, the most violent disturbance of the atom of which we have any knowledge is that accompanying the ejection of a high speed electron. It is natural to regard this as the probable source, direct or indirect, of the characteristic X-radiation. Investigation completely confirms this view.

# Independence of Electron after Expulsion.

There is considerable and apparently conclusive evidence that the electrons after expulsion take no part in the process of radiation\*—that is, the process of emission of the characteristic radiation as ordinarily detected. They must, of course, on encountering other atoms, give rise to some radiation—this, however, is not the fluorescent radiation which is emitted in such intensity as that observed. That this is so follows from the following considerations:—

As the exciting primary radiation becomes more penetrating (of shorter wavelength), the speed with which electrons are emitted from a substance exposed to this primary radiation becomes greater, whereas the fluorescent radiation remains homogeneous and unchanged in character. Now all experiments on the production of X-rays show that as the speed of the generating cathode rays increases, although an intense homogeneous X-radiation may be emitted, there is emitted also a heterogeneous radiation of comparable intensity, which becomes more penetrating. No such heterogeneity or change in penetrating power is observable in the fluorescent radiation.

Again, the ionizing power of the fluorescent radiation is comparable with—in limiting cases it is equal to—that of the secondary corpuscular radiation. This corpuscular radiation cannot then produce the fluorescent X-radiation by any process subsequent to expulsion, for all experiments on the relation between the ionizing power of cathode rays and of the X-rays they produce show that only a small fraction of the ionizing power goes into the resulting X-radiation.

Again, if the fluorescent X-radiation was produced by electrons subsequent to their expulsion from the parent atoms, there could be no distinction between the effectiveness of various groups of electrons provided they had the same velocity. Yet the intensity of the fluorescent X-radiation is most distinctly related not to the whole number but only to a particular group of electrons in the corpuscular radiation.

Direct experiments made by Charman† in order to determine whether the nature of the substance subsequently bombarded by the electrons had any influence upon the

<sup>\*</sup> BARKLA, 'Proc. Camb. Phil. Soc.,' May, 1909.

<sup>†</sup> CHAPMAN and PIPER, 'Phil. Mag.,' June, 1910; CHAPMAN, 'Phil. Mag.,' April, 1911; 'Phil. Mag.,' March, 1913.

when the greater portion of the energy of the expelled electrons, even in excess of that essential to the production of the fluorescent radiation, was absorbed in a second substance, the intensity of the fluorescent X-radiation was the same as when the electrons were completely stopped by the substance originally emitting them.

There appears to be no escape from the conclusion that the emission of fluorescent X-radiation is completely independent of the career of electrons subsequent to their expulsion from the atoms.

As ionization is produced by expelled electrons constituting the corpuscular radiation, it follows that the simple process of ionization is not accompanied by X-ray fluorescence.

# Independence of Electron During or Preceding Expulsion.

It does not appear possible that the expelled electron is itself the source of this radiation during the final simple process of ejection, that is, during the final unidirectional flight which carries it beyond the bounds of the atom, for the homogeneous fluorescent X-radiation is both independent of the velocity of expulsion of these electrons, and thus of the period of actual escape, and according to our conception of homogeneous radiation implies a regular vibration.

Again, the vibration of the electron (which is finally expelled from an atom) or of other components of a normal atom when under the influence of a primary Röntgen radiation must of course depend in character upon the primary radiation and be ultimately of the same frequency. This forced vibration would produce a radiation with properties dependent upon and possibly ultimately identical with those of the primary radiation. Such a radiation, due to the forced vibration of electrons within the atom, is actually emitted; it however constitutes the scattered X-radiation.

On the other hand, the fluorescent X-radiation is characteristic not of the exciting primary radiation, but of the excited substance; it cannot be produced by such a controlled motion but only by a free vibration. The emission of a fluorescent radiation, too, is not general but conditional, that is to say, some special atomic condition appears to be essential to the production of the fluorescent radiation. We know that vibrations are produced within the atom both by Röntgen radiations of longer wavelength, and by the impact of electrons moving more slowly than the velocity critical to the production of a particular characteristic X-radiation; yet the characteristic radiation has never been observed in these cases.

We thus arrive at the conclusion that the fluorescent X-radiation is due to a free vibration occurring within the atom when in an abnormal state—probably after the ejection of a high speed electron.\*

<sup>\*</sup> See Barkla, "Der Stand der Forschung über die sekundare Röntgenstrahlung" ('Jahrb. d. Radioaktivität und Elektronik,' April, 1908).

Each Fluorescent X-radiation Associated with Particular Group of Electrons.

But of the electrons emitted with a velocity greater than the critical velocity, that is, with energy greater than that of a quantum of the fluorescent X-radiation, only a fraction are accompanied by the particular fluorescent radiation, say of series K.\*

As pointed out, the total corpuscular radiation, though consisting of electrons ejected with one velocity, may be divided into several distinct portions, each portion being definitely associated with the emission of fluorescent radiation of a definite series. the whole corpuscular radiation consists of K† electrons, associated with the emission of the characteristic X-radiation of series K, L electrons associated with the characteristic X-radiation of series L, and M, N, &c., electrons presumably associated with the emission of hypothetical lower frequency characteristic X-radiations of series When few K electrons are emitted, the K fluorescent X-radiation is very weak; when K electrons increase in number the intensity of the fluorescent X-radiation (series K) increases, and indeed, as we shall see, there is certainly approximate if not perfectly accurate proportionality between the number of K electrons ejected and the intensity of the fluorescent X-radiation of series K. On the other hand, there is no simple relation between the intensity of fluorescent radiation of a particular series and the total number or energy of the electrons in the whole corpuscular radiation.

\*Connection with Absorption of Primary Radiation and with Corpuscular Radiation (Radiation in Quanta).

It has been seen that of the energy definitely absorbed in association with the emission of fluorescent X-radiation of series K—K absorption—the fraction remitted as fluorescent radiation (series K) is at its maximum value when the primary radiation is of just shorter wave-length than the fluorescent radiation itself, and that this fraction decreases with a decrease in wave-length of the primary radiation. Thus if  $F_K$  is the energy of the fluorescent radiation (series K)  $\mu$  and  $\mu_K$  are the wavelengths of the primary and fluorescent radiations respectively, then as  $\mu$  decreases from  $\mu_K$  downward  $F_K/E_K$  decreases from about half, as shown in fig. 5.

On the other hand, as  $\mu$  decreases from  $\mu_{K}$  downward, of the energy  $E_{K}$  specially absorbed in connection with the emission of K radiation, an increasing fraction re-appears as energy of corpuscular radiation ( $C_{K}$ ). In the case of the one substance examined in detail, and approximately in that of other substances,  $C_{K}/E_{K}$  increases from about  $\frac{1}{2}$  towards 1. Thus when  $\mu$  is just less than  $\mu_{K}$  the energy of the primary radiation specially absorbed is approximately equally divided between the two types of secondary

<sup>\*</sup> See Barkla, "Charakteristische Röntgenstrahlungen" (Verh. d. Deut. Phys. Gesell., 1913).

The case here considered is that in which the "J" radiation (which from most elements is of very high frequency) is not excited.

radiation; that is, for a given quantity of corpuscular radiation emitted, there is emitted sufficient K fluorescent radiation to produce an equal ionization. But as the K fluorescent radiation in this case differs little from the primary radiation, we see that for each K electron emitted there is also produced sufficient fluorescent radiation to set free another high speed electron with a velocity only just smaller than that of the electron ejected directly. As this electron possesses the energy of a quantum of the fluorescent radiation, we conclude that for each K electron emitted directly there is emitted also one quantum of the K fluorescent radiation. This experimental conclusion is so definite, so simple and significant, that we shall proceed to study the relations under other conditions. But before doing so we must again point out the extreme improbability of such an agreement by chance; à priori the energy of fluorescent radiation might be that of 100 quanta or  $\frac{1}{100}$  part of a quantum for each electron emitted, yet it is one quantum within a small possible error.

As the wave-length  $\mu$  of primary radiation decreases, the energy of a quantum of this primary radiation increases, but the quantum of the characteristic radiation remains constant. If, therefore, one quantum of this characteristic radiation is still emitted for each high-speed electron emitted, then

 $\frac{\text{Energy of K fluorescent X-radiation}}{\text{Energy of K corpuscular radiation}} = \frac{\text{quantum of K fluorescent radiation}}{\text{quantum of primary radiation}}$ 

$$= \frac{\text{frequency of K fluorescent radiation}}{\text{frequency of primary radiation}} = \frac{n_{\text{K}}}{n} \text{ or } \frac{\mu}{\mu_{\text{K}}},$$

i.e., the energy of the fluorescent radiation becomes a smaller and smaller fraction of that of the corpuscular radiation. This is exactly what happens, and certainly approximately at the theoretical rate.

Possibly this argument is clearer as follows:

Total energy of K fluorescent radiation  $(F_K)$ Energy of a quantum of K fluorescent radiation  $(hn_K)$ 

= Number of quanta of fluorescent radiation (N<sub>F</sub> say),

Total energy of K corpuscular radiation  $(C_K)$ Energy of a quantum of primary X-radiation (hn)

= Number of electrons in corpuscular radiation (N<sub>c</sub> say).

Hence the number of quanta of fluorescent radiation emitted per electron of the corpuscular radiation =  $\frac{N_F}{N_C} = \frac{F_K}{C_K} \frac{n}{n_K}$ .

The experimentally determined number of quanta of fluorescent radiation emitted for each electron in the corpuscular radiation—i.e.  $\left(\frac{\mathbf{F}_{\kappa}}{\mathbf{C}_{\kappa}}\frac{n}{n_{\kappa}}\right)$ —is given in the following table (V.) for primary radiations of various wave-lengths. These results show that

one quantum of K radiation is emitted for each K electron expelled whatever be the velocity of its ejection.

Table V.

	4
Approximate wave-length of primary X-radiation.	Number of quanta of K fluorescent radiation emitted per K electron ejected.
$\frac{\text{cm.}}{0.87 \times 10^{-8}}$	1:09
$0.71 \times 10^{-8}$	0.95
$0.56 \times 10^{-8}$ $0.49 \times 10^{-8}$	0·85 0·81
$0.35 \times 10^{-8}$	0.30

The variations from unity are irregular and obviously may be the result of observational or experimental errors. The maximum variation of 19 per cent. is small considering the number and nature of the experimental determinations involved. Apart from a quantum theory, the range of possible values is so enormous in comparison with the variation observed that the emission of one quantum of characteristic X-radiation for each electron in the associated corpuscular radiation must be regarded as an experimentally established fact. It is a fact of some significance.

Less accurate experiments on other substances lead to a similar conclusion approximately if not accurately. There is no reason to think the results would be less convincing. The fundamental physical truth one cannot for a moment question, though it is possible that certain conditions would produce greater irregularities than are exhibited above.

# First Approximation to Energy Relations.

If the two K secondary radiations—the corpuscular and the characteristic X-radiation—together accounted for the whole of the K energy absorbed, we should have of the energy of the primary beam absorbed as K absorption, the fraction  $\frac{n}{n+n_{\rm K}}$  or  $\left(\frac{\mu_{\rm K}}{\mu+\mu_{\rm K}}\right)$  re-emitted as K corpuscular radiation, and the fraction  $\frac{n_{\rm K}}{n+n_{\rm K}}$  or  $\left(\frac{\mu}{\mu+\mu_{\rm K}}\right)$  as K fluorescent X-radiation.

It has been shown that when  $\mu$  is somewhat less than  $\mu_{\rm K}$ , i.e., when  $\mu=0.84\mu_{\rm K}$ , about 42 per cent. of the energy of the primary radiation specially absorbed in bromine appears to be re-emitted as fluorescent X-radiation of series K, while about 46 per cent. is re-emitted in the K corpuscular radiation. Thus the two together account for about 88 per cent. of the primary radiation. Also as  $\mu$  diminishes, the two energies of fluorescent and corpuscular radiations remain approximately complementary, the energy of the former diminishing while that of the other increases. Table VI. gives the experimentally determined values of

K fluorescent radiation (energy)
K primary absorption (energy)

and Total K secondary radiation (energy)

K absorption (energy)

K absorption (energy)

in columns II., IV. and VI. along with the simple theoretical values for the first two  $\frac{n_{\rm K}}{n+n_{\rm K}}$  and  $\frac{n}{n+n_{\rm K}}$  in columns III. and V. The agreement between the values in columns II., IV. and VI. with those in columns III., V., and with unity respectively, is certainly sufficiently close to permit us to say that these simple energy relations express the experimental facts exceedingly well for a first approximation. It should be observed that the recorded values are not simply relative values; each one is the result of an absolute determination in the sense that it is independent of the others, and might have had any value less than unity. There appears to be little loss of energy within the atom, but what there is appears most marked when  $\mu$  is just less than  $\mu_{\rm K}$ . The values of  $\frac{n_{\rm K}}{n+n_{\rm K}}$  and  $\frac{n}{n+n_{\rm K}}$  are plotted against wave-lengths of primary radiation in fig. 5 where they are indicated by the broken curves.

Table VI.

I.	II.	III.	IV.	V.	VI.
Approximate wave-length.	K fluorescent radiation (energy). K primary absorption (energy).	$\frac{n_{\mathrm{IC}}}{n+n_{\mathrm{IC}}}$	K corpuscular radiation (energy). K primary absorption (energy)	$\frac{n}{n+n_{\mathrm{IL}}}$	K fluorescent + corpuscular radiation (energy). K primary absorption (energy)
cm. $0.87 \times 10^{-8}$ $0.71 \times 10^{-8}$ $0.56 \times 10^{-8}$ $0.49 \times 10^{-8}$ $0.35 \times 10^{-8}$	0.42 $0.36$ $0.31$ $0.29$ $0.23$	0.46 $0.41$ $0.35$ $0.32$ $0.26$	$0.46 \\ 0.55 \\ 0.66 \\ 0.75 \\ 0.76$	0.54 $0.59$ $0.65$ $0.68$ $0.74$	0.88 0.91 0.97 1.04 0.99

It should, however, be pointed out that in elements of lower atomic weight a considerably smaller fraction of the energy of primary radiation appears to be transformed into fluorescent (characteristic) X-radiation. Measurements of the energy of corpuscular radiation, too, indicate a smaller fraction transformed into radiation of this type than is the case in bromine. Thus experiments point to a marked loss of energy in such substances.\*

With elements of higher atomic weight, however, there appears to be a close approximation of the experimental values with those given by the above simple theory.

We shall, in what follows, deal principally with the results obtained with ethyl bromide, the behaviour of which is certainly typical of many substances. If in light elements, as seems probable, a considerable portion of the energy absorbed is unaccounted for, this is a matter for future investigation. It does not, however, affect the conclusions to be obtained with other substances, but indicates that the conditions are not the simplest possible.

## Process of Radiation.

It is inconceivable that the processes resulting in the emission of fluorescent X-radiation and corpuscular radiation are either independent or even that they are alternative conclusions (dependent on some critical condition in the atom) to similar initial processes. The above experimental relations are inexplicable on any such assumption. The emission of each electron of the corpuscular radiation is associated with the emission of a quantum of the corresponding fluorescent X-radiation. But we have already shown that the electron after emission takes no part in the fluorescence, so are left with the conclusion that the atom which emits an electron emits also a fluorescent radiation characteristic of the atom itself. We shall now consider the process in greater detail.

The above approximate relations show that the energy of primary radiation absorbed per K electron expelled is greater than that per lower frequency electron expelled by a quantum of K radiation.† In the measurements upon which this conclusion is based we are unable to distinguish between L, M, and N electrons, but as L electrons constitute quite 80 per cent. of the whole, and for the others the energy

- \* Further experimental work on the light elements is desirable, for it is remarkable that such a variation should occur with a comparatively small variation in the atomic weight of the radiating substance (fig. 4), for the line spectra of these elements are similar, and in addition the absorption curves (as in fig. 2) are exactly similar. Similar absorption curves indicate similar processes of absorption.
- † If we ignore the first approximation altogether and examine the experimentally determined values of Energy absorption per K electron energy absorption per L electron , we see that the possible error is energy of quantum of K radiation necessarily very great. The experimental values 1.4, 1.15, 0.9, 0.7 and 0.9 are of the order of magnitude of unity.

absorption does not differ greatly from that for the L electrons, we may class them all as L electrons. As all electrons leave the atom with the same velocity, and as the emission of the fluorescent radiation is subsequent to the absorption of primary radiation, we may express the fact in the following way:—The energy of a quantum of K radiation is the energy required to move an electron from the position and state of a K electron to the position and state of a lower frequency electron, an L electron. (We are led to regard a K electron as being situated nearer to the centre of the atom than the lower frequency electrons, and, in general, the frequency of vibration of electrons to be in the order of their distance from the surface. Thus the J, K, L, M electrons are arranged in this order from the centre outwards.)

But when a K electron is hurled out of the atom, it is possible that, for stability, another electron will fall into the position and state of the K electron. If it falls from the position and state of an L electron, the energy of a quantum of K radiation must be re-emitted. The emission of a quantum of K radiation for each electron expelled we have found to be an experimental fact.

Reasoning by analogy, we conclude that to displace an L electron necessitates the absorption of the energy of one quantum of L radiation more than that required to eject a still lower frequency electron. This energy is re-emitted as a quantum of L radiation when an electron falls from the position and state of one of these lower frequency electrons to the position and state of the displaced L electron.

Thus, on this hypothesis, the energy of primary radiation absorbed per K electron emitted is  $h(n+n_{\rm K}+n_{\rm L}+n_{\rm M}+...)$ , i.e., the sum of the kinetic energy of the ejected electron, which is hn, and the energy of one quantum of each of the characteristic X-radiations of series K, L, M, .... Similarly, the energy absorbed per L electron emitted is  $h(n+n_{\rm L}+n_{\rm M}...)$ , and so on.

If, after a K electron is ejected, its place is taken by an L electron, and the place of that by an M electron, and so on, then for each K electron ejected there is emitted one quantum of each of the K, L, M, ... X-radiations.

In this case the fraction  $\frac{\text{energy of } K \text{ characteristic } X\text{-radiation}}{\text{energy of } K \text{ corpuscular radiation}}$ , i.e.  $\frac{F_K}{C_K}$  is equal to  $\frac{n_K}{n} \left( \text{or } \frac{\mu}{\mu_K} \right)$  as before. But what has previously been regarded as purely K corpuscular radiation is K corpuscular radiation together with a weak corpuscular radiation produced by the re-absorption of the L, M, ... characteristic X-radiations emitted in association with the K corpuscles. That is, if there be additional L characteristic radiation associated with the emission of K corpuscles, the ionization produced by its absorption must be added to that produced more directly by the K corpuscular radiation. Thus more accurately our comparison of the energies of fluorescent and corpuscular radiations has given

K characteristic X-radiation (energy)
K corpuscular radiation + L characteristic radiation accompanying K electrons (energy)

and this should be compared with the theoretical value  $\frac{n_{\rm K}}{n+n_{\rm L}}$ . The values in Table V. should in this case be multiplied by  $\frac{n+n_{\rm L}}{n}$  to give the number of quanta of K radiation emitted per K electron ejected. They then become 1.22, 1.04, 0.92, 0.86, and 0.94.

The fraction  $\frac{\text{K characteristic X-radiation (energy)}}{\text{K primary absorption (energy)}}$  on this theory is equal to  $\frac{n_{\text{K}}}{n+n_{\text{K}}+n_{\text{L}}+\dots}$  (see Table VII., columns II. and III.); and

 $\frac{\text{K corpuscular radiation (energy)}}{\text{K primary absorption (energy)}} \, \text{equals} \, \frac{n}{n + n_{\text{K}} + n_{\text{L}} + \dots}.$ 

Table VII.

I.	II.	III.	IV.	V.	VI.
Approximate wave-length ( $K\alpha_1$ line).	K fluorescent radiation (energy)  K primary absorption (energy)	$\frac{n_{\mathrm{K}}}{n+n_{\mathrm{K}}+n_{\mathrm{L}}\dots}.$	K corpuscular radiation + L characteristic radiation with K electron (*).  K primary absorption (energy)	$\frac{n+n_{\rm L}}{n+n_{\rm K}+n_{\rm L}}.$	K secondary radiations (energy)  K absorption (energy)
cm. $0.87 \times 10^{-8}$ $0.71 \times 10^{-8}$ $0.56 \times 10^{-8}$ $0.49 \times 10^{-8}$ $0.35 \times 10^{-8}$	0.42 $0.36$ $0.31$ $0.29$ $0.23$	0.43 $0.38$ $0.33$ $0.31$ $0.25$	0.46 $0.55$ $0.66$ $0.75$ $0.76$	0.57 $0.62$ $0.67$ $0.69$ $0.75$	0·88 0·91 0·97 1·04 0·99

But again, what we have observed is in this case

K corpuscular radiation + L characteristic radiation accompanying K electrons (energy)

K primary absorption (energy)

which should accordingly be compared with  $\frac{n+n_{\rm L}}{n+n_{\rm K}+n_{\rm L}+\dots}$ , as in columns IV. and V.

In column VI. the total energy of secondary radiations associated with the emission of K electrons is expressed as a fraction of the K absorption, as in Table VI., column VI.

The agreement between theory and experiment, as shown in Table VII., is, on the whole, very close.

The experimentally observed energy relations, however, are not sufficiently accurate to enable us to determine with certainty the exact process by which the original configuration of the atom is regained.

In fundamentals, however, the theory can scarcely be questioned. It explains so many facts and is so simple in itself that there seems no alternative but to accept it in outline at least.

[The principal facts which may be regarded as giving support to the theory may be summarised as follows:—

- (1) When  $\mu$  is just less than  $\mu_K$  for any one of the heavier elements, the fraction of the primary energy absorbed (K absorption) transformed into K characteristic radiation  $\left(\frac{F_K}{F_{nr}}\right)$  is slightly less than 0.5.
  - (2) There is evidently a limiting value of about 0.5 for the fraction.
  - (3) As  $\mu$  diminishes this fraction invariably diminishes.
- (4) In the one substance carefully investigated—a substance giving the maximum value just below 0.5—the rate of diminution of this fraction with diminution in  $\mu$  is almost perfectly that given by theory.
- (5) When  $\mu$  is just less than  $\mu_K$  for the one substance thoroughly investigated, the fraction of primary energy absorbed (K absorption) transformed into K corpuscular radiation  $\left(\frac{C_K}{E_K}\right)$  is also slightly less than 0.5. This is approximately true for many substances, though a value appreciably but not considerably less than
  - (6) The value exceeding 0.5 has never been observed.
  - (7) As  $\mu$  diminishes, the fraction invariably increases.
- (8) In the one substance investigated, the rate of increase of the fraction is approximately the theoretical rate when  $\mu$  is not near to  $\mu_{K}$ . (But when  $\mu$  is near to  $\mu_{K}$  there is probably a real deficiency of corpuscular radiation.)
  - (9) There is no evidence against the theory in its essentials.
  - (10) The theory is a very simple one.

0.5 has been obtained.

Experiments were commenced with Mr. Shearer with the object of determining whether the emission of K electrons was accompanied by a weak L radiation additional to that associated with L electrons, but the investigation was interfered with by war work, and did not get beyond the preliminary stage. The intensity was, however, seen to be very small. Theory as indicated above would lead us to

expect that such an L radiation would at most account for only 7 per cent. of the K absorption, for  $n_{\rm L}$  is only about  $\frac{1}{7}n_{\rm K}$ . If no such additional L radiation is discovered, the natural conclusion is that the displaced K electrons are replaced by electrons of still lower frequency or possibly, though highly improbably, from outside the atom.

It is possible that there are not electrons of every series in every atom of the same substance, or, if there are, they may not be in the best position to enable them to replace an electron of an adjacent higher series. If, for instance, a K electron were ejected from an atom which did not contain an L electron, or in which the L electron was situated on the other side of the centre, its place might be taken by an M electron, with the result that the energy emitted as characteristic radiation would be equal to that of one quantum of K radiation + one quantum of L radiation. This would be equal to one quantum of radiation of slightly greater frequency than what we have previously regarded as the K radiation, and might account for a neighbouring spectral line in the K radiation.

The origin of various spectral lines in a particular series (say the K series) was first explained by Kossel as the result of electrons falling from the various outer rings into the K ring, and was not given in the early communications of the writer.\* According to Kossel, the  $K_{\alpha}$  radiation is that emitted when an electron falls from the L ring into the K ring;  $K_{\beta}$  that resulting from the fall from the M ring into the K ring, and so on. In support of this he shows that the necessary energy relations hold. Thus the energy emitted when an electron falls from the M ring into the K ring is the sum of the energies of fall from the M ring into the L ring, and from the L ring into the K ring; what Kossel shows is that  $hn_{K_{\beta}} = hn_{L_{\alpha}} + hn_{K_{\alpha}}$ , that is, one quantum of  $K_{\beta}$  radiation possesses the sum of the energies of one quantum of  $L_{\alpha}$  radiation and one quantum of  $K_{\alpha}$  radiation. This indicates that, while the fall of electrons takes place between consecutive rings, it sometimes takes place across an intermediate ring position.

These observed relations thus confirm the conclusion to which the writer was led in a most direct manner from measurements of the energies of corpuscular and fluorescent (characteristic) radiations and their relation with the associated absorption of primary radiation.

The experiments described above lead to the conclusion that a characteristic radiation (of series K, say) is probably emitted when an outer electron falls into the position of a displaced K electron, the energy previously absorbed in displacing the K electron in excess of that carried away as kinetic energy being now re-emitted as a quantum of K radiation, or, what seems more probable, as a quantum of K radiation accompanied by quanta of lower frequency radiations.

<sup>\*</sup> Sir Ernest Rutherford kindly sent a copy of Kossel's paper to the writer a few weeks after the publication of the preliminary notes in 'Nature,' drawing attention to some similarity of eonelusion. This paper was evidently published some time previous to the writer's notes.

## Quantum Theory.

In the above investigation of the energy transformations accompanying the phenomenon of X-ray fluorescence the results of greatest significance in their bearing on the quantum theory are probably the following:—

- (1) The energy absorbed per K electron expelled is greater than that per L electron expelled by the energy of one quantum of K radiation approximately. This leads to the statement that the energy of a quantum of K radiation is that which must be absorbed to displace a K electron from its normal position and state to the position and state of an L electron.
  - (2) A quantum of K radiation is emitted for each K electron ejected.
- (3) The number of electrons in the secondary corpuscular radiation plus the number of quanta of fluorescent X-radiation, that is, the total number of electrons emitted by the direct action of the primary X-radiation together with those emitted indirectly through the agency of the associated fluorescent X-radiation is not equal to the number of quanta of primary radiation absorbed, but varies from equality with to double that number. Thus if, for the sake of clearness, we regard the first approximation as being accurately true, N quanta of primary radiation cause the emission of

 $\frac{1}{2}$ N electrons (directly)+ $\frac{1}{2}$ N (indirectly through the fluorescent radiation) when  $\mu$  is just less than  $\mu_{K}$ ,

 $\frac{2}{3}$ N (directly) +  $\frac{2}{3}$ N (indirectly) when  $\mu$  is  $\frac{1}{2}\mu_{K}$ ,

N (directly) + N (indirectly) when  $\mu$  is very small,

or, in general,

$$N \frac{\mu_K}{\mu + \mu_K}$$
 (directly) +  $\frac{\mu_K}{\mu + \mu_K}$  N (indirectly) for any value of  $\mu$ .\*

Thus, contrary to what has sometimes been supposed, the energy of a quantum does not persist through these energy transformations as an indivisible entity.

(4) If we consider the energy absorbed by each atom from which a K electron is expelled, we see that when  $\mu$  is just less than  $\mu_{K}$ , approximately two quanta of primary radiation are absorbed per atom,

when  $\mu = \frac{1}{2}\mu_{\rm K}$ ,  $1\frac{1}{2}$  quanta of primary radiation are absorbed per atom,

$$,, \quad \mu = \frac{1}{4}\mu_{K}, 1\frac{1}{4} \quad ,, \qquad . \quad , \qquad , \qquad , \qquad ,$$

or, in general,

when 
$$\mu = f\mu_{K}$$
,  $(1+f)$  ,, ,, ,, ,,

\* If there are L, M, ... characteristic X-radiations associated with the emission of K electrons—indicated above as a possibility—the number of electrons emitted will be greater than is given by this expression; in this case it will depend on the number of series (K, L, M, ...) of characteristic radiations.

Consequently the number of quanta of radiation absorbed per atom (i.e., per absorbing atom) varies from about two to just more than one as the wave-length of primary radiation diminishes from just less than  $\mu_{\rm K}$  to a very small quantity. A quantum is a quantity of radiation evidence of the absorption of which has not been obtained. Frequently however—when  $\mu$  is a small fraction of  $\mu_{\rm K}$ —the absorption per atom approximates to the energy of a quantum.

It should be pointed out that the last two conclusions concerning the quantum theory, although expressed in precise terms, are in no way dependent on a close agreement between the experimental results and those given as a first approximation.

# A NEW SERIES OF CHARACTERISTIC RADIATIONS. (J SERIES.)

A marked deviation of the experimental results from what was expected on the above theory has led to the discovery of a new series of characteristic X-radiations.\* From light elements these newly-found radiations are of only moderate penetrating power, but are much "harder" (of shorter wave-length) than the K radiations emitted by these same elements; they are of the same order of wave-length as the K radiations from the heavier elements—silver, tin, &c. The irregularity was found in the relation between the energy of K corpuscular radiation and the K absorption of the primary beam (p. 331). Thus it appeared that the fraction K corpuscular radiation (energy) increased with the diminution of wave-length of K primary absorption (energy) the primary radiation only up to a certain wave-length; beyond this there was a sudden diminution in its value. This result, however, was based on the assumption that the ionization in air was produced by electrons of a definite number of groups, K, L, M, &c., throughout the whole range of wave-lengths employed: in other words, it was assumed that within this range of wave-lengths there was no radiation characteristic of the elements nitrogen and oxygen, consequently that no fresh group of electrons was emitted as corpuscular radiation as the wave-length of the primary radiation was reduced.

Thus it will be observed that the values given in column IX. of Table III. depend upon the ratio ionization coefficient in air absorption coefficient in air. But the value of the absorption coefficient in air for the radiations of shorter wave-length were obtained by simple proportion from those in aluminium after the subtraction of the scattering coefficient,

<sup>\*</sup> There has been some evidence of this for many years. The writer in 1903 found that unless the primary radiation was kept "soft" an additional radiation of some kind was emitted by substances of low atomic weight. It was also observed that to obtain evidence of the most perfect scattering from light elements as shown by polarization experiments "soft" radiation had to be used. Again, experiments on the distribution of scattered radiation showed that this approximated to that for the fluorescent radiation when the primary radiation was not very "soft." These and other experiments suggested the possible emission of a characteristic radiation of another series.

that is, they were based on the absorption laws on the assumption that air had no spectral line within this range of wave-lengths. An unobserved spectral line would involve greater absorption on the shorter wave-length side, and would be accompanied by increased ionization. The ionization was, of course, experimentally observed; but this was originally thought to be that accompanying what might be termed normal absorption in air. A greater absorption would necessitate a correction of the values obtained and would account for the apparent discrepancy.

The existence of a characteristic X-radiation may, however, be shown by various methods—by experiments on (a) X-ray fluorescence (excitation by a primary X-radiation); (b) corpuscular radiation; (c) ionization; (d) absorption. All these methods have been applied and the results have demonstrated the existence of a series of X-radiations previously unknown; the absorbabilities (consequently the wave-lengths) of these radiations from several elements have been determined.

[The experiments, the results of which are given under the headings (b), (c), and (d) of this section, were undertaken in collaboration with Miss M. P. White, whom I also wish to thank for help in the preparation of diagrams and tables for the lecture. The results briefly referred to in section (a) were obtained during an investigation with Miss J. Dunlop of the scattered radiation. A more detailed account of these investigations will be published later.]

## Ionization Method.

Experiments showed that with a primary radiation of decreasing wave-length the value of ionization coefficient in  $C_2H_5Br$  failed to increase at the expected rate beyond a wave-length of about  $0.56 \times 10^{-8}$  cm. It was evident, however, that the emission of a characteristic radiation from air would be accompanied by a rise of the air ionization and consequent fall of the ratio. Experiments were therefore made upon the ionization in sulphur dioxide and methyl iodide relative to air, in order to determine whether the sudden change occurred in the ethyl bromide ionization or in the air ionization.

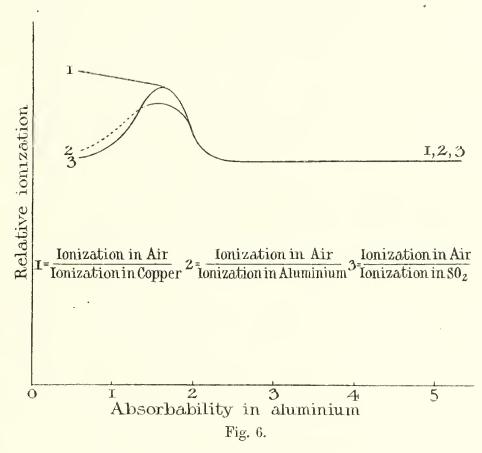
The ionization coefficient in sulphur dioxide had been shown to bear an approximately constant ratio to that in air through a long range of wave-lengths.\* The range of wave-lengths employed had, however, not included that at which the observed change occurred. On extending the series of experiments it was found that the ratio ionization coefficient in SO<sub>2</sub> underwent a diminution at the same wave-ionization coefficient in air

length as had given a low value for  $\frac{\text{ionization coefficient in } C_2H_5Br}{\text{ionization coefficient in air}}$ . A similar effect was observed in comparing the methyl iodide and air ionization coefficients.

<sup>\*</sup> Barkla, 'Proc. Camb. Phil. Soc.,' May, 1909; 'Phil. Mag.,' August, 1910; Barkla and Philpot, 'Phil. Mag.,' June, 1913.

It was evident then that the sudden change was due to an increase in the ionization in air, and was such as would be given if nitrogen gave an X-ray spectral line of absorbability in aluminium  $(\lambda/\rho)_{\Lambda 1}$  equal to about 2.5, or wave-length about  $0.56 \times 10^{-8}$  cm.

On continuing the SO<sub>2</sub> ionization experiments with X-rays of shorter wave-length still, the ratio of ionizations rose again. This effect indicated that sulphur emits a characteristic X-radiation of shorter wave-length than that from nitrogen and oxygen (as might be expected from analogy with the K and L series of radiations), and as the primary radiation became of shorter wave-length than the radiation characteristic of sulphur, this characteristic radiation was excited, and was accompanied by the corresponding corpuscular radiation from that substance producing an increased ionization in sulphur dioxide. The rise and fall of the ratio ionization in  $SO_2$ , with decreasing wave-length or increasing penetrating power is shown in fig. 6, curve 3.



Corpuscular Radiation Method.

To obtain further confirmation of this, it was decided to compare the ionization in aluminium with that in air. As the ionization can only be directly measured when the substance is in the gaseous state, the method adopted was of necessity an indirect one. Ionization is usually produced by the high speed electrons from a gas passing through the same gas. Instead of this the electrons from aluminium were allowed to

pass through hydrogen (the direct ionization in which is negligible), and this indirect ionization was measured. Though the ionization produced in hydrogen by the secondary corpuscular radiation is not necessarily quite the same as that produced in aluminium by the absorption of its own corpuscles, the factor giving aluminium ionization from that in hydrogen is constant or nearly so. Consequently changes in the *relative* values of the ionization in aluminium and air may be observed equally well by this indirect method.

The ionization in a chamber with its back face of aluminium and filled with hydrogen was compared with that produced by the same beam of X-rays in air. In the first case the ionization was ionization by the electrons ejected from hydrogen plus that by the net gain of electrons from aluminium at the end. In the second case the ionization was produced by electrons from the air itself plus that produced by electrons from aluminium ends. Approximately these are (a) ionization in hydrogen by electrons from the aluminium plates, and (b) ionization in air by its own electrons plus a comparatively small ionization in air by a net gain of electrons from the aluminium plates at the end of the chamber. (The latter of these might have been approximately eliminated from the results of experiments on the corpuscular radiation from aluminium. This was unnecessary, however; an approximate correction was obtained by extrapolation.)

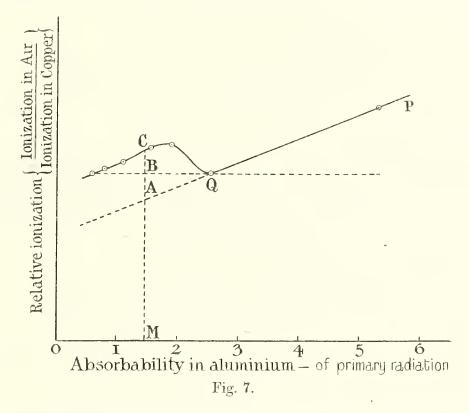
Homogeneous beams of various wave-lengths were employed, and the relative ionizations in air and in aluminium were obtained. A correction had, however, to be made to the relative ionizations obtained in this way, for the air ionization was due to the electrons ejected from a given mass of air, whereas the aluminium ionization was produced by the electrons from a mass which increased with the frequency of the primary radiation. This is due to the fact that the shorter the wave-length of the primary radiation, the greater is the velocity of electrons which this radiation ejects, consequently the greater is the depth of material from which they emerge. An approximate correction for this may, however, be found by extrapolation. This is explained below in its application to the determination of the relative ionizations in air and in copper. The final results of the experiments on air and aluminium are shown graphically in fig. 6, curve 2. The rise in the air ionization at a wave-length about  $0.56 \times 10^{-8}$  cm. ( $\lambda/\rho$  in Al = 2.5) is well marked, and the subsequent rise in aluminium ionization is shown in the change in relative ionization in the opposite direction at a wave-length of about  $0.52 \times 10^{-8}$  cm. ( $\lambda/\rho$  in Al = 1.9). It will be seen that the curve so obtained is very like the relative ionization curves for SO<sub>2</sub> and air obtained directly. This, of course, is as it should be, the atomic weights of aluminium and sulphur being close together, and their characteristic radiations consequently being of neighbouring wave-length. The difference between the two indicates that the radiation characteristic of sulphur is more penetrating than that of aluminium, for the relative ionization begins to approach the normal value with more penetrating primary radiation (of shorter wave-length) in the case of sulphur than that of

aluminium. This means that the special additional corpuscular radiation is excited in sulphur only by primary radiation slightly more penetrating than that necessary to excite the corresponding corpuscular radiation in aluminium.

In order to obtain the ionization in a substance of atomic weight differing considerably from that of nitrogen and oxygen, and thus to get rid of the effect of the neighbouring spectral line in one of the ionized substances, the ionization in copper was compared with that in air by the same method as in the case of aluminium and air.

The uncorrected results for the ratio  $\frac{\text{ionization in air}}{\text{ionization in copper}}$  are shown graphically in





emerge is seen in the downward slope of the curve with decreasing wave-length of the primary radiation; but for this effect the line should be approximately horizontal.

Producing the relative ionization line PQ towards the left we get the relative ionization if there had been no additional corpuscular radiation associated with the spectral lines of nitrogen and oxygen. Thus the ordinate at C should be multiplied by the ratio  $\frac{MB}{MA}$  to bring it to the true relative value of the ionization for a primary radiation of absorbability OM.

Treating the values in this way we get the curve 1, fig. 6, giving the relative ionizations in air and copper for various radiations.

The shape of the curve shows that the explanation given in the above cases is the correct one; for beyond the wave-length  $0.56 \times 10^{-8}$  ( $\lambda/\rho$  in Al = 2.5) the value of

ionization in air rises with diminution of wave-length, and with further diminution there is no return of the relative ionizations to the original value.\* Thus the ionization in air increases beyond the spectral lines of air; but there is no rise of the ionization in copper, as there is no spectral line characteristic of copper within the range of wave-lengths used. The ionizations in aluminium and sulphur dioxide relative to that in copper may be obtained by division from the values more directly determined and plotted in fig. 6; the results are given in fig. 8, from which we see

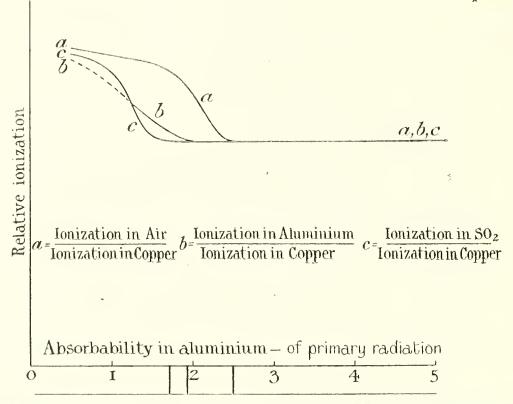


Fig. 8. Showing approximate positions of the J spectral lines of N, Al, and S obtained from relative ionization curves.

more clearly that these radiations characteristic of air, aluminium and sulphur, are progressively more penetrating. The J spectral lines for nitrogen, aluminium and sulphur obtained from these curves are shown at the foot of the figure. A similar increase of penetrating power with atomic weight of radiating substance had been found to hold among the radiations of series K and L.

A point worthy of notice is that with primary radiation of much shorter wavelength than those of the characteristic radiations (J series) of the substances compared, the relative ionization is approximately the same as that obtained when

\* The last two values in Table III., column IV., giving  $\frac{\text{ionization coefficient in C}_2\text{H}_5\text{Br}}{\text{ionization coefficient in air (K, L, ...)}}$  were corrected by the factors 1·32 and 1·39 respectively, because the observed ionization in air was partially due to J electrons. To obtain the ionization in air due to K, L, ... electrons alone, the observed total ionization had to be multiplied by  $\frac{\text{AM}}{\text{CM}}$  (fig. 7), or the above fractions had to be multiplied by  $\frac{\text{CM}}{\text{AM}}$ , which had values 1·32 and 1·39 in the two cases.

the primary radiations were of longer wave-length than these characteristic radiations. This denotes that the number of J electrons emitted from air bears the same ratio to the total number of electrons (K, L, M, &c.) emitted by air as is the case from aluminium or sulphur.

#### Fluorescence Method.

The more direct method of demonstrating the existence of a characteristic radiation is to excite it by a primary radiation of shorter wave-length and observe it in the secondary radiation emitted. The secondary radiation emitted by the substance and detected by an electroscope in many cases is very approximately a homogeneous radiation; in others a second (softer) characteristic radiation must be filtered out by absorbing sheets before the homogeneity of the radiation can be demonstrated; in other cases again, the scattered radiation produces considerable effects and cannot be filtered out, but in this the effect of the scattered radiation can be calculated and eliminated. The last method was used by BARKLA and NICOL,\* and was afterwards applied by CHAPMAN† to substances of highest atomic weight. In this case the whole of the secondary radiation emitted by a substance was compared with that emitted by another substance whose secondary radiation under the condition of the experiment was almost purely a scattered radiation.

In experimenting upon light elements this scattered radiation becomes a very important factor, and the elimination of the effect of this from the whole secondary radiation becomes very difficult. For our present purpose it is sufficient to show that in addition to scattered radiation a characteristic X-radiation is emitted by the light elements. As scattering substances, paper, paraffin wax, and aluminium were used. It had previously been shown that X-radiations differing considerably in wavelength are scattered to an equal extent by these light elements, and that scattering takes place without appreciable change of type. The introduction of a fluorescent characteristic radiation into the secondary radiation from one of these light elements would be shown by an increase in the total intensity of secondary radiation, and by a change in its penetrating power.

A primary radiation of varying wave-length was directed on to a sheet of paper, paraffin wax, or aluminium, and the ratio between the intensities of the primary and secondary radiations was observed by means of two electroscopes, while the absorbabilities of both primary and secondary radiations were tested by screens of aluminium. It was found (1) that the intensity of the secondary radiation rose and fell as the wave-length of the primary radiation was diminished in the same way as did that of a characteristic radiation; (2) the penetrating power of the secondary radiation varied as it would by the superposition on the scattered radiation of a homogeneous characteristic radiation of intensity varying as above; (3) in aluminium the

<sup>\* &#</sup>x27;Proc. Phys. Soc. Lond.,' September, 1911.

<sup>† &#</sup>x27;Roy. Soc. Proc.,' February, 1912.

characteristic of aluminium.

corresponding features all occurred with radiation of shorter wave-length than in paper and paraffin wax which consisted of lighter elements.

In these experiments comparatively heterogeneous primary beams were used, so that the particular absorbability or wave-length at which the characteristic radiations appeared could not be determined with any accuracy. The absorbability in aluminium, however, was of the order of magnitude of that obtained more exactly by other methods.

# Absorption Method.

It has been shown that over the range of wave-lengths between those of the spectral lines of two consecutive series and not near to the longer wave-length series, the absorptions in any pair of substances are in an approximately constant ratio for any wave-length. Any marked deviation from proportionality in the absorptions in two substances as the wave-length of the radiation changes, shows the existence of a characteristic radiation. Thus as the wave-length of a radiation diminishes, the fraction absorption in substance A remains approximately constant until the radiation becomes of shorter wave-length than that of a radiation characteristic of A or B. In this case the corresponding absorption increases rapidly and the ratio of absorptions is changed. The absorptions of homogeneous radiations were therefore determined in iron and aluminium, so as to provide a further test of the existence of a radiation

Passing from long waves to shorter, the ratio  $\frac{\text{absorption in Fe}}{\text{absorption in Al}}$  suddenly rises at wave-length approximately  $1.9 \times 10^{-8}$  cm., which agrees with the determined wave-length of the K radiation of iron (fig. 9). There is, further, a sudden drop in the ratio,

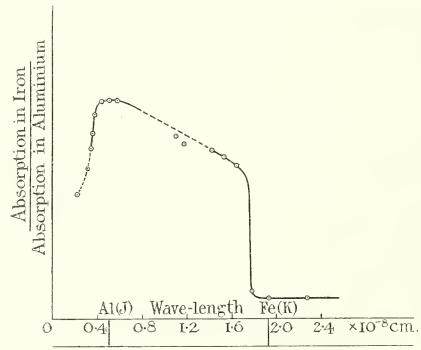


Fig. 9. Showing approximate wave-lengths of the K radiation from Fe and the J radiation from Al from relative absorption curve.

or rise in the absorption in Al for a wave-length of  $0.5 \times 10^{-8}$  cm. approximately, which again shows that Al has a characteristic radiation of about the same penetrating power as that of the K radiation from tin.

Thus all the methods, direct and indirect, show that under the usual conditions the light elements emit characteristic radiations of moderate penetrating power, and that the higher the atomic weight of an element, the more penetrating is its radiation. As these radiations are very much harder (of shorter wave-length) than those of the K series in the lighter elements, it is evident that they constitute a new series of characteristic radiations; and as there is no evidence of an intermediate series, this series should be called the J series. The mass absorption coefficients in Al  $(\lambda/\rho)_{Al}$  for the radiations from N to S vary from about 2.5 to 1.75, or the wave-lengths from 0.56 to 0.5 × 10<sup>-8</sup> cm. approximately.\*

#### PRIMARY X-RADIATION.

The theory of emission of characteristic X-rays outlined above should also be extended to the process of production of X-rays by the incidence of cathode rays on any material, as in the ordinary X-ray tube. For it has been shown by Beatty† that the generation of a radiation of given penetrating power or frequency necessitates the incidence of electrons with energy greater than that of a quantum of that radiation. This applies not only to the production of radiation which is evidently characteristic of the particular anti-cathode employed, but to that heterogeneous radiation which becomes more and more penetrating as the speed of the exciting cathode rays increases. Such a law indicates a similarity in the process of production of all the X-rays generated in the anti-cathode. If mere collision between an electron of the cathode stream and an atom or a component of an atom in the anti-cathode resulted in the generation of X-rays, the resultant radiation consisting of all kinds of pulses produced by random collisions would possess the properties of a mixture of homogeneous radiations but without such a definite superior limit to the frequency of its components as has been actually observed. The definite law indicates a definite process, a process similar in essentials to that described in connection with the production of the characteristic X-radiations.

There is no reason to deny that what has usually been regarded as the method of production of X-rays is inoperative; the probability is rather that the electromagnetic radiation generated in an anti-cathode by the random collision of the exciting cathode particles is of small intensity; it does not constitute the bulk of the radiation recognised as X-radiation. (Yet a complete theory must take account of the experimental fact of a decided polarization in the primary beam—indicating an

<sup>\* [</sup>These values are probably rather high, as they were obtained by comparison of the wave-length of the α line with the absorbability of the whole K-radiation.—August, 1917.]

<sup>† &#</sup>x27;Roy. Soc. Proc.,' 1912.

amount of polarized radiation which ought very easily to have been observed in Beatty's experiments if it differed in method of production from that of the bulk of the heterogeneous primary radiation.)

If in the phenomenon of X-ray fluorescence we find it is essential that an electron be displaced from its normal position, and are led to conclude that X-rays are produced when the displaced or some other electron falls back into this position, we ought to look for a similar process in explanation of the more direct generation of X-rays. This naturally leads to the following considerations:—

The cathode particles in the cathode stream by collision expel electrons from their normal positions in the atoms in the anti-cathode; these displaced electrons thus receive an amount of energy—measured from the normal position and state—which must be less than the original kinetic energy of the impinging electron and may be much less. When they fall back to their normal positions they re-emit as radiation the potential energy which they lose in the fall. Further, if an electron in falling from one definite position to another emits radiation whose frequency n is given by the relation hn = energy lost in falling from position to position—a law for which we have given direct experimental evidence and which was assumed by Bohr—we need only assume an extension of the law to apply to any fall within the atom. We must assume that when an electron falls from any position within an atom to some normally stable position it emits radiation, a quantum of which is equal to the potential energy lost in the fall.

Thus when an electron falls back from its position of greatest displacement, the frequency of the resultant radiation is given by hn = potential energy of electron in its position of greatest displacement measured from its normal position and state—which may have any value less than the original kinetic energy of the cathode particle. When it happens that the place of the displaced electron is taken by an electron from one of the outer rings in the atom, a characteristic radiation is emitted.

Such a mixture of heterogeneous and characteristic radiations is actually emitted from the anti-cathode. This theory suggest a definite upper limit to the penetrating power or frequency of the radiation possibly emitted by an anti-cathode, for the highest frequency would be that generated when an electron falls freely from the surface of the atom to the innermost stable position of an electron, on the assumption that such a limit exists. A limit to the frequency of the X-radiation generated in a particular anti-cathode has not yet been proved, nor is there any certain experimental evidence in support of the hypothesis, though from considerations indicated above it seems probable theoretically.

[Though results have been obtained by certain experimenters which from a superficial examination appear to indicate such a limit, these results might have been foretold not only qualitatively, but with fair accuracy quantitatively, from the observed laws of scattering and absorption.

An approximate limit to the penetrating power of a radiation does not indicate a

limit to the frequency or wave-length, for the absorption of penetrating radiations is principally due to the process called scattering, the laws governing which are entirely different from the laws of absorption connected with the emission of electrons. The process of scattering imposes the limit on penetrating power, and where scattering varies little with wave-length, gives the appearance of an approximate limit to that wave-length. Such a small variation of absorbability with a variation of wave-length (as measured by absorption in heavy substances) has been observed in the region for which results have been given.

Again, an empirical formula which connects wave-length and penetrating power, when absorption is due to one process, can scarcely be expected to hold when absorption is due to an entirely different process and is governed by entirely different laws.

In addition, since the discovery of the J series of radiations of higher frequency than those of the K series (see p. 349), it seems highly probable that radiations of higher frequency than that of the radiation supposed to have been observed can be generated, for this has been indicated as belonging to the K series.

For these reasons we think that further evidence will be needed in support of such conclusions, though results of the same kind may perhaps be expected elsewhere.]

## GENERAL CONCLUSIONS UPON X-RADIATION AND THE QUANTUM THEORY.

Thus all the available evidence shows that X-radiation may be and is emitted by electrons—probably in certain cases by groups of electrons, or even atoms—as a continuous process and in any quantity whatever. It is frequently emitted in quantities almost infinitesimal in comparison with a quantum. It is, however, emitted in quanta from atoms when certain critical conditions resulting in the ejection of certain electrons are reached, the process of radiation then taking place in a perfectly definite manner involving the radiation of a definite amount of energy which is proportional to the frequency of vibration.

Absorption, too, normally takes place in very minute quantities—very small in comparison with a quantum. But in certain processes, which usually account for nearly the whole absorption, the radiation is absorbed in quantities greater than a quantum of the primary radiation, quantities varying with the conditions from one to two quanta approximately. There is no evidence of absorption of X-radiation in whole quanta, though the conditions are frequently such as to give an approximation to this.

All this evidence seems to indicate that a quantum of radiation in the sense in which it has frequently been used, *i.e.*, as an indivisible bundle of radiant energy, does not exist. The process of radiation may be, and is, continuous—at any rate, within limits extending to far smaller quantities than the quantum. The quantum is a unit of atomic energy which must be absorbed to change the configuration of

the atom, and is radiated when that configuration returns to its original state. It thus of necessity appears in certain processes of absorption and radiation.\*

The results obtained by certain experimenters on the ordinary production of primary X-radiation suggest, too, that mere collision of electrons with an anti-cathode is not sufficiently sudden, or of sufficiently violent a nature, to result in the production of the X-rays as ordinarily detected. The probability is rather that the function of the cathode particle is to displace electrons from their normal positions in atoms of the anti-cathode, and thus to produce in these atoms vibrations—some characteristic, others not—which result in the emission of the primary radiation.

\* There is no need to indicate the problems of absorption and radiation still awaiting solution. Though there is no evidence as to the nature of the mechanism involved in these processes beyond what is indicated by a change from certain initial to certain final conditions these investigations seem to establish many important facts, and to show the narrow limits within which the quantum theory is in any sense applicable.

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# X. A Critical Study of Spectral Series.—Part IV. The Structure of Spark Spectra.

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Received May 18,—Read June 1, 1916.

[PLATES 4-18.]

THE spectrum of an element produced by the electric spark is in general fundamentally different from that produced by the arc. The latter is marked by the predominance of groups of lines forming series associated with one another, and by lines related to these series in definite ways. In the former very few series have been discovered, the lines are very much more numerous, and the great majority are weak. Both kinds vary very much according to the way in which they are produced, and this is specially the case with spectra produced by the spark. Even when they are produced by similar methods by different observers—as, for instance, by Eder and VALENTA, and by EXNER and HASCHEK—there will be found a large number in one not included in the other and vice versa. It is even questionable whether it is possible to draw a distinct and definite line of demarcation between the two, e.g., in the cases of Cu and Ba, to take two instances; the arc spectra—with very numerous lines—in many respects have analogies with those of the spark. But very little is known as to the structure of the latter, beyond the fact that in some of them sets of lines with the same frequency differences are met with. The present communication is an attempt to throw some light on this question.

The material at disposal is so vast that it is necessary to limit the discussion to a few elements, and even in them to restrict it to certain relations only. The elements selected are silver and gold. It had originally been intended to include also copper and barium as illustrating the transition from one to the other kind of spectra. But their inclusion would have rendered the present communication unduly long, whilst their omission enables us to confine the discussion to the elaboration of a single principle. The reason for the selection is that the author has had occasion to study with special care for other purposes the spectra of Ag and Ba, whilst those of Au and Cu—belonging to the same group as Ag—were specially investigated to see if the results afforded by Ag were supported by them. That of Cu was also interesting, as in the arc there are a very large number of doublets and triplets discovered by Rydberg; indeed the origins of some of the frequency differences observed were first

suggested by the case of Cu in which their values are comparatively small. But it required the support of the larger values afforded by Ag and Au to firmly establish the relations. Similar relations have been found in many other elements. The spectra of the rare gases from Ne to RaEm are built on a precisely similar plan, and in fact a map for some of the Kr lines was drawn many years ago on the plan of those given here for Ag and Au, although at that time the origin of the differences was not known.

The notation used is that of previous papers in this series. The letters p(m), s(m) are used to denote the sequences  $N/(m+f)^2$  which in the alkalies give the variable parts of the Principal and Sharp series. The wave-numbers of the Principal series are then s(1)-p(m) and of the Sharp p(1)-s(m). The doublet separations are due to denominator differences denoted by  $\Delta$ , say m+f and  $m+f-\Delta$ . The quantity  $\Delta$  is a multiple of the oun,  $\delta_1 = 90^{\circ}47 \,\mathrm{W}^2$ , where  $100 \,\mathrm{W}$  is the atomic weight. As however the quantity  $\delta = 4\delta_1$  occurs very frequently, this is generally used. When  $x\delta$  is added to the denominator in either of these sequences a new line is produced, and it is said to be laterally displaced. Thus, P(m) denoting any line, if  $x\delta$  is added to the variable part (the term in m), the new line is written  $P(m)(x\delta)$ , but if added to the constant term (the limit) it is written  $P(m)(x\delta)$ . Regarded from this point of view the two sets of a doublet series are regarded the one as a displacement of the other. Thus  $P_2(m) = P_1(m)(-\Delta)$ ;  $S_2(m) = (-\Delta)S_1(m)$ ;  $D_{12}(m) = D_{11}(m)(-x\delta)$ ;  $D_{22}(m) = (-\Delta)D_{11}(m)(-x\delta)$ .\*

In the following, for the sake of shortness, when p, s are used alone they stand for the limits p(1), s(1). Line separations are always given in thick type, and, in general, the decimals of wave-numbers are omitted.

It will be seen later that the structure of the spectra depends on long series of constant differences in wave-numbers (or frequencies). As the total number of lines in a particular spectrum is very great there will always be a certain number of chance agreements for any given difference. In forming an opinion as to the reality of the connection indicated by a given set of such differences it will then be necessary to obtain an estimate of the number of such coincidences to be expected, on the supposition that the lines form a purely chance distribution. Owing to observation errors exact differences will never occur. Suppose that the difference being investigated lies between  $n \pm x$ , where x is a small quantity, and suppose that the spectrum under consideration contains p lines whose wave-numbers lie between  $N_1$  and  $N_2$ ,  $N_1 < N_2$ . The average separation between successive lines will be  $(N_2-N_1)/(p-1)$ . The chance of one falling in the space 2x is therefore  $2x(p-1)/(N_2-N_1)$ . Taking each number in succession from the smallest, this is the chance of finding a line  $n \pm x$  ahead of it. But clearly we must stop when we reach a value  $N_2-n$ . The probable number of lines contained in this region is  $n(p-1)/(N_2-N_1)$  and the probable total

<sup>\*</sup> There is reason to believe, however, that the series  $P_2(m)$  and the satellites are the normal lines, and that  $P_1(m)$  should be written  $P_2(m)(\Delta)$ ;  $D_{11}(m) = D_{12}(m)(x\delta)$ , &c.

number of lines available for pairs is  $p-n(p-1)/(N_2-N_1) = \{1-n/(N_2-N_1)\}p$ , since p is a very large number. Hence the probable number of coincidences will be

$$\left(1 - \frac{n}{\mathbf{N_2} - \mathbf{N_1}}\right) p \, \frac{2px}{\mathbf{N_2} - \mathbf{N_1}} \, \cdot$$

This is the number if we know that the distribution is a wholly chance one. If, however, the frequencies are known to be based on certain constant differences the numbers found with differences which are not sums or differences of multiples of these constants will not occur. Hence, in this case, the above calculated probable number will be too large. It therefore must be regarded as a maximum value, and that the chance coincidences will be fewer than the value given by it.

The first difference to be tested was naturally that of the ordinary doublet separation  $\nu = p(-\Delta)-p$ . In the case of Cu a very frequent difference found was about 1000. This is rather larger than  $4\nu$  and it suggests that as  $\nu$  is formed by the displacement  $-\Delta$  on p, the new difference is formed by the displacement  $-4\Delta$ . But the calculated value of  $p(-4\Delta)-p$  is too great. The value of  $p(-3\Delta)-p(\Delta)$ , however, comes to 999.75, which is practically exact. This is the difference of the two displacements  $-2\Delta$  and  $2\Delta$  on  $p_2$ , that is of symmetrical displacements on either side of  $p_2$ , which latter is probably more fundamental than  $p_1$ . The corresponding values for Ag and Au were also found to occur in large numbers in their respective spectra. This large difference naturally suggested a search for the intermediate ones  $p-p(\Delta)$ ,  $p(-2\Delta)-p(-\Delta)$ ,  $p(-3\Delta)-p(-2\Delta)$ , which were duly found as well as others given by  $s-s(\Delta)$ ,  $s(-\Delta)-s$ .

There are also certain others depending on the d sequence and the satellite separations, but these latter are not considered in the present paper.

It is to be noted that if, for instance, the wave-number of a line is given by n = p - X, the addition  $p(-\Delta) - p$  simply displaces the line to  $(-\Delta)n$ . If, however, it be subtracted, the new wave-number is  $2p - p(-\Delta) - X$  and a normal displacement does not occur. As will be seen later there are numerous instances of displacements of the first kind.

The method adopted in attacking the spectrum of a given element was first to make a list of the wave-numbers in a vertical column of ascending values downwards. In order to test a given difference each number in succession was tested, and when a coincidence was found pencil lines were drawn down and up with the actual difference found entered. As a rule values were entered when different from that being tested by two or three units or more. The result was a maze of pencil lines, many of the wave-numbers having as many as five or six attached to them. The next step was to start from some particular wave-number and make a new list following up the pencil lines from one to another. In this way a set would be isolated from the general list, all connected together in parallel and series groupings with one another but showing no connection with the other wave-numbers. In most cases the number of individuals

in a set was found to be very large and it is only possible to visualize their mutual connection by exhibiting them on a diagram. They appeared connected to one another by links of a few definite species. It will be convenient to refer to these sets as linkages, and a constant difference as a link. The vast majority of the spark lines are thus connected. As a rule the linkages are attached to—or related to—one of the ordinary series lines. It will be convenient for shortness of statement to denote the various links by definite letters. The following will be used—

$$p-p(\Delta) = a, p(-2\Delta)-p(-\Delta) = c,$$

$$p(-\Delta)-p = b, p(-3\Delta)-p(\Delta) = d,$$

$$s-s(\Delta) = u, s(-\Delta)-s = v.$$

From the constitution of a linkage it is clear that if p-X denote the wave-number of the first—or any one—of the linkages, that of another can be expressed in the form—

Wave-number = 
$$-X + xp(\Delta) + yp + zp(-\Delta) + x^{1}p(-2\Delta) + y^{1}p(-3\Delta) + \xi s(\Delta) + \eta s + \xi s(-\Delta)$$

where x, y, z... are integers. From the way in which the links appear as the difference of two terms the sum x+y+... must be odd. The existence of lines in which this sum is even is not excluded, as the method adopted would not isolate them and no attempt has been made to test for them. Tables for certain of these linkages are given below. We now proceed to give the evidence on which the above statements are made.

The data for p, s,  $\Delta$ ,  $\delta$  are taken from Part III. of this series of papers.\* They are:—

	Ąg.	Au.
$p = 8(\infty)$	$30644.60 + \xi$	$29465^{\circ}18 + \xi$
	$= N/(1.891897)^2$	$= N/(1.929298)^3$
$s = P(\infty)$	$61116.33 + \xi$	$70638.12 + \xi$
•	$= N/(1.339600)^2$	$= N/(1.246047)^2$
ν	$920^{\circ}435 - {}^{\circ}0014\xi$	3815.54
$\Delta$	$27786^{\circ}57 - 1^{\circ}29\xi$	$113961 - 5.46\xi$
δ	$421.0087 - 0196\xi$	$1406.93 - 047 \xi$

The values of the different links as calculated from these are as follows:—

$\alpha$	880.77	3195.14
b	920.44	3815.54
c	962.54	4607.77
d	1007:26	5635:33
e	3771.00	17253.78
14	2458.64	11342:19
v	2616.61	14937.24

<sup>\* &#</sup>x27;Phil. Trans.,' A, vol. 213.

The exact values of these links depend only slightly on the exactness of the values of the limits, for if the latter change by  $\xi$ ,  $\Delta$  also changes with it in such a way that the consequent changes in the links are only small. For instance even with the large values of Au, the links  $a \dots e$  become a+0, b+0,  $c-03\xi$ ,  $d-07\xi$ ,  $e-08\xi$ . The links u, v, however, depending on a limit which does not affect  $\Delta$ , show larger, although still small, variations, viz., u of  $-24\xi$  and v of  $-8\xi$ .

In the case of Ag, the greatest and least values of the wave-numbers tested are  $N_2 = 50611$ ,  $N_1 = 15691$ , whilst the total number of lines is p = 600. Substituting these values in the formula given above the number of probable coincidences with a given link  $n \pm x$  is

$$20x\left(1-\frac{n}{35000}\right)$$

The corresponding values for Au are  $N_2 = 53697$ ,  $N_1 = 15923$ , p = 750, whence the probable number of coincidences is

$$29.8x\left(1-\frac{n}{38000}\right)$$

In order to form a judgment on the question whether the observed coincidences are due to a real effect or to mere chance, the series of curves Ag 1-7 (Plate 4) and Au 8-14 (Plate 5) have been drawn. The actual observed differences are represented as abscissæ, a dot being placed for each case. For any particular difference, the number of dots within x on either side of it are counted and entered as an ordinate. Joining the tops, we get a broken curve which represents the frequency of occurrence of the various values of an observed link. A dotted horizontal straight line drawn at a distance above the line of abscissæ, calculated from the above formula, gives the probable frequency on the supposition that the values are due to pure chance. curves are drawn for the two cases of x = 4 and 1. The curves for the long e links are made to cover a wider region than the others for a reason considered below. The v link for Au has also been extended further in order to see how the observed differences behave when they are away from the immediate neighbourhood of the As is seen, their frequency is much less than the calculated chance, in agreement with the reasoning given above that the chance distribution must be less than that given by the formula. In the Ag set the curves show that the four small links, a, b, c, d are clearly systematic, with numbers more than twice the maximum probable on chance and practically agreeing in value with the calculated results. The three larger links also show the same effect with the distinction that they appear to be arranged, about three maxima, roughly two units apart for u, v, and three units for e, with e = 3771 itself actually at a minimum. In Au, the existence of peaks is even more marked. They are probably all real effects and indicate that certain small displacements will often simultaneously occur with the change of link.

The existence of observation errors will flatten out any peaks if they exist in the

frequency curves 1...14 given above. An estimate of the magnitude of the effect to be thus expected is difficult, not only because we have estimated maximum errors by Kayser and Runge alone for the arc lines, but because frequently an observed difference has to be taken between measurements by two observers whose systematic errors may be different.

The evidence for the reality of the variation in a link is based on the existence of long series of the same link. The following are a few examples out of many others.

In Silver—

- (1) 30514 **2460·39** 32974 **2460·84** 35435 **2461·00** 37896 **2457·26** 40353.
- (2) 17814 3772·32 21591 3779·86 25371 3778·01 29194 3778·56 32928.
- (3) 30959 3776·44 34735 3777·47 38513 3773·79 42286 2618·00 44904 3767·59 48672.

In Gold—

(4) 15293 **5634·92** 21558 **5633·23** 27191 **5631·12** 32822 **5635·29** 38457 **5639·46** 44097 41320

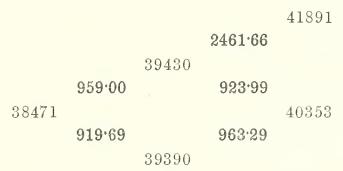
		3192:47		3197.75.			
(5)	38127				44517	3200.04	47717
		3197.76		3192.46.			
			41325				
(6)	33784	3194.86	36979	3197.04	40176	3196.71	43372.

The first three indicate without any doubt that the links about 2460 and 3778 are real effects, and they show that they cannot be explained by errors of observation, for if so, the extreme lines would have to be affected with errors beyond any possibility. For instance, in (2), the differences refer clearly to one about 3778.4 and individual errors of small amount assigned to the lines will make the differences all equal to this. But if the link is supposed to be the calculated 3771, the errors in the extreme lines would have to be 29.7 distributed between them—a value manifestly too large. The existence of these variations is also shown clearly by (5) (see p. 367). The origin of these variations is discussed below in more detail.

The probability curves offer incontestable evidence that the existence of these links is not due to chance coincidences. But other evidence is available. The fact that the vast majority of the spark lines are thus connected can be explained in no other way. A glance at the maps of the linkages given below, and consideration of the way in which the links are combined, are convincing that although some of the links shown are certainly due to coincidences the linkage effect is a real one. Amongst such peculiarities may be mentioned the long sequences of the same link referred to above, the existence of numerous meshes and congeries of meshes, of parallel sequences, repetitions, &c. A few of these are exhibited in diagrammatic form in Plate 6.

They are excerpted from the maps of some of the linkages given later. In these the dots represent wave-numbers of spectral lines, the small circle corresponds to the wave-number which is given in the notes to the figures, and the letters denote the links. We shall call a collocation of four lines connected in parallel—as for example the two sets in fig. (a)—a mesh. The number of these is very large and the Au spectrum contains some very complicated examples.

In a very large number of cases a correction on a single line will render all the links attached to it correct. Thus, for instance, in the AgP (ii.) and (iii.) maps, the line 42203 (see fig. l, Plate 6) differs from two preceding lines by 964.89, 2818.83 and from two succeeding lines by 959.62, 2456.44. If this be corrected by -2.2 ( $d\lambda = .12$ ) the differences become the links 962.69, 2616.63, 961.82, 2458.64—practically exact. Another example may be taken from the line 40353, which occurs in the first of the long sequences given on p. 366. In addition to the link 2457.26 there shown, it forms part of a mesh which may be written:—



If 39430 be 3.5 larger ( $d\lambda = -.23$ ) the three links converging on it are made simultaneously exact, viz., 962.50, 920.49, 2458.41, the outstanding variations being only small fractions of possible observation errors. The u link also becomes the same as that just before 40353 in the long sequence to which the abnormal 2460 of the others have returned. In these two instances the first may be due either to an observation error or to another cause. The second, however, is too large to be explained as due to an error, but is probably due to the same cause that produces the double peaks in the frequency curves. That such causes exist has been already pointed out by the many long sequences of equal and abnormal links. As additional evidence the following examples out of a large number of similar ones may be taken. In the AuX linkage the following mesh occurs—

		41320		
	3192.47		3197.75	
38127				44517
	3197.76		3192.46	
		41325		

Here alterations of 2.6 ( $d\lambda = -.15$ ) on 41320 and -2.6 on 41325 make the differences two exact- $\alpha$  links. But it would also make the two lines coincide, whilst

they are given clearly by Eder and Valenta as two  $\lambda\lambda = 2419^{\circ}41$ , '10, so that any supposition as to the presence of observation errors is ruled out of court. There is therefore a displacement either in the links themselves or in a line 41322'6.

The other example is from silver, in the AgS (3) linkage, viz.,

31815

2455.51

34271

6.79

2461.79

30846 **963·16** 31809.

Here again the two u links deviate from their normal values by equal amounts 3.1. Their mean is 2458.66, which is exact. The two lines 31815, 31809 are  $\lambda\lambda = 3142.82$ , 20 and are clearly displacements by equal amounts in opposite directions from 3142.51.

The number of cases similar to the above in which a change in one wave-number will make a number of abnormal links all conform to their typical values is extremely large. When two such links occur in series—both in the same direction—I refer to them as series inequalities; when in parallel, or one additive and the other subtractive, as parallel inequalities. If one is too large and the other too small by equal amounts, it means that when in series, the line between them is displaced from the first one, and the third has this displacement annulled. If in parallel it means that the third line receives the same displacement over the second that the second received over the first. If, however, the two links differ from their normal values by the same amount the above changes are reversed.

In certain cases, especially where D linkages are involved, the nature of the displacement would seem obvious — where, for instance, the irregularity can be explained by a change from a  $D_{11}$  type to a  $D_{12}$  or vice versû. Thus in the AgD (4) linkage the line 33192 is 2620'19 greater than the line 30572. The former depends (see No. 7 of the AgD (4) Table) on D<sub>12</sub>. The satellite separation is 2.69 by observation. Thus link v + change from  $D_{12}$  to  $D_{11}$  is 2616.61 + 2.69 = 2619.30, leaving .89 ( $d\lambda = .08$ ) to be distributed between observations of the two lines and of the satellite separation. The first line is  $p(-2\Delta)-s(\Delta)+s-VD_{12}(4)$ , the second would then become  $p(-2\Delta)-s(\Delta)+s(-\Delta)-VD_{11}$  (4). A similar explanation is possible for the previous example from the AgS (3) linkage. The line 31815 contains – VS (3) in its Now VS (3) =  $9231.23 = N/(3.446862)^2$ , a displacement of  $-6\delta_1$  on this produces a separation 3.36. So that numerically 34271 is 31815  $(-6\delta_1) + u + 22$  $(d\lambda = -0.02)$ , and 31809 is 31815  $(-1.3\delta_1)$  -11  $(d\lambda = 0.01)$ . Such explanation, however, is not so plausible as in the preceding case, for the S sequences do not seem to be so susceptible of small displacements as the D. The most frequently occurring irregularities, however, cannot be explained in this way for the P(1) linkages show

them of the same value as the others, and the smallest displacement of  $\delta_1$  on VP(1) produces separations of far too high a value. It is necessary to look for some cause which will produce variations of from 2 to 10 in all cases. Such a cause would be small variations in N. The condition is also fulfilled if, instead of making the links depend on displacement operations by  $\Delta$  on p, s, the operations are made on values of p, s, already displaced by small multiples of  $\delta_1$  or  $\delta$ . For example,  $a' = -p(x\delta + \Delta) + p(x\delta)$ ,  $b' = -p(x\delta) + p(x\delta - \Delta)$ , &c. The calculated changes are found to be as follows:—

	Ag (with $x\delta$ ).	Au (with $x\delta_1$ ).
a'-a	-61x	-1.7x
b'-b	-61x	-2.17x
c'-c	- 66x	-2.75x
d'-d	71x	-3.63x
e'-e	-2.59x	-10.25x
u'-u	-2.25x	-9.17x
v'-v	-2.47x	-13.32x

The x refer to multiples of  $\delta$  for Ag and of  $\delta_1$  for Au. The reason for the difference of treatment is that where those of  $\delta_1$  might occur in Ag the change would be much smaller than the observation errors, whilst if any of  $\delta$  occurred in Au the changes would be larger than those included in our purview. In constituting the formulæ for the lines of certain linkages carried out below this method has been adopted, when the variations are too large to be ascribed to errors. This assumption, however, must not be considered to be adopted as the real explanation. This is left open. The use of the assumption enables the dependence of the lines on the p and s terms to be shown conveniently in tables. At the same time it exhibits clearly the presence of these small disturbances when existing, whatever their real cause may be. In many cases also after appearing in the tables for certain lines they disappear again for succeeding lines, and so have assisted in locating the latter.

In the case of the long link e, which is the sum of the four short p links, it might be expected that some indication of the nature of this displacement might be given by considering how the e, or the enlarged e links depend on the displaced small links a, b, c, d. The number of the e links being large, and the number of possible arrangements of the small links within it being 4!, the labour of testing them is so great that a complete discussion has not been attempted. The chief difficulty is that only a few of the small links in them are normal so that the others do not appear in the general lists of links, and the whole spectra have to be examined afresh. In the case of the AgS (3) and AgD (4) linkages no complete sets were found. In the AuP (1) of the links beginning at 25736, 20100, 37357, 41172, 26236, 43497 (see map AuP), complete sets were found for 26236 only. In the AuS (3) of those beginning at 25387, 20776 (S<sub>1</sub> 3), 23805, 24592 (S<sub>2</sub> 3), 27783, 30109, 24477 (see map AuS (3)),

all but the last gave sets, but only by admitting values of links so abnormal that they were not counted in the general list. Also in the AuY linkage the sets beginning at 17788, 28152 were found to exist. They are reproduced here:—

1.	26236 .			. 17260			43497
	3830.99	30067	4601.44	34669	5636.00	40305	3192:35
2.	25387 .			. 17256			42644
	5640.57	31028	4606:31	35634	3821.55	39456	3188.54
3.	20776 .			. 17262			38038
	3189.54	23966	3817:32	27783	5647:31	33431	4607:51
4.	23805 .			. 17258			41064
	3195.78	27001	3822:33	30823	5618.55	36442	4621.83
	3810.21	27615	4604.05	32219	3194.83	35414	5640.40
5.	24592 .			. 17263	3.13		41855
	3191.06	27783	5647.81	33431	4607.51	38038	3816.78
6.	27783 .			. 17260	. 17		45043
	5647.81	33431	4607.51	38038	3816.78	41855	3188.07
7.	30109 .			. 17252			47361
	3194.64	33303	5621.20	38924	4598.98	43523	38 <b>3</b> 8
8.	17788 .			. 17256	3.26		35045
	3813.90	21601	4608.08	26209	5639.11	31848	3196.09
9(a).	28152 .			. 17260	)· <b>4</b> 9		45412
	3815.65	31967	4610.61	36578	5637.59	42216	3196.67
9 (b).	28155 .			. 17257	·32		45412
	3814.60	31970	4608.46	36578	5637.59	42216	3196.67

An examination of the above shows that, with the exception of Nos. 8 and 9 from AuY, all contain very abnormal links. It is noticeable also that in all except 3 and 4 the links occur in cyclic order backwards or forwards of a, b, c, d, viz.: (1) b, c, d, a; (2) d, c, b, a; (5) a, d, c, b; (6) d, c, b, a; (7) a, d, c, b; (8) b, c, d, a; (9) b, c, d, a; whilst in (3) the order is a, b, d, c, and in (4) a, b, d, c, or b, c, a, d. In (1) 30067 has no link in the general list. In (2) 39456 has not been attached to any linkage and the other two belong to the X and Y linkages. In (3) all are included in the S (3). No. (4) shows two possible sets both contravening the cyclic rule. If the links shown are real displaced links the two sets form a complete cycle like that in fig. e of Plate 6. But 36442 belongs to the Y linkage, whilst in the second the three intermediate lines belong to other linkages. It is probable, therefore, that both sets in No. 4 are spurious. Nos. 3, 5 and 6 have portions in common. In (7) the last two intermediate belong to the X and Y linkages. The set is therefore probably spurious. Nos. 8 and 9 show all good links whilst 9 shows that two c links are possible but 31970

is an arc line. Apparently, therefore, there is only good evidence for all the intermediate links in Nos. 1, 3, 5, 6, 8 and 9. In applying the displacement rule to the e links in the formulæ lists given below the numerical values allowed are supposed to be e = 17253.78 and  $e(-\delta_1) = 17264.03$ —in other words, e is taken as an independent link and not as the composite a+b+c+d. If it is composite each of the a, b, c, d may be modified, and values of e intermediate to 17253 and 17264 may enter. If then the wave-numbers were known accurately to unity  $(d\lambda = .5)$  for long waves to '05 for short) these ought to serve as tests of the kind of displacement supposed. Take, for instance, (3) as an example. It is seen that e = 17262.04 $= e(-\delta_1)-2$ , and the small separations are  $\alpha(3\delta_1)-54$ ,  $b(-\delta_1)-39$ ,  $d(-3\delta_1)+159$ , c-26. Thus if e is really composite it should equal  $a(3\delta_1)+b(-\delta_1)+d(-3\delta_1)+c$ , and its value should be '40 larger—i.e., it is already correct within very small error limits. If, however, it is independent, the link 5647, which is just as far as it can be from  $d(-3\delta_1)$  or  $d(-4\delta_1)$ , would be spurious, 23966 and 27783 would be linked to 20776 and 33431 to 38038, and the error -2 in the long link would be divided between observation errors on 20776 and 38038, say 20776 - 43 and 38038+1.57, giving respectively  $d\lambda = 10$  and -11. All this argument, however, goes on the assumption that only one displacement can take place at each step. Thus in passing from 27783 to 33431 the existing  $a(3\delta_1)$  may displace to  $a(-\delta_1)$  and the d link be  $d(-\delta_1)$ , producing a line '90 ( $d\lambda = 0.08$ ) less than that observed. The next link would be  $c(-\delta_1)$  when 38038 is corrected by 2 and then the transformation to  $e(-\delta_1)$  is completed. That these double displacements take place is not unlikely since the successive lines in our lists may be quite independent of the neighbouring lines, the chain links merely serving as a sort of Ariadne's thread to discover them.

A corresponding treatment for all the sets gives:—

In the above the value of  $d\lambda$  is the correction to be applied to the last line to make the long link e or  $e(-\delta_1)$  exact supposing the whole error thrown on that line alone. In 9a, 9b only are there indications that the small links show displacements the same as those given to e, but this cannot be the case for both sets as the two last links must be the same. The discussion of the cause of the enlarged links must therefore be left open until more accurate measurements are attainable.

There are a large number of more or less parallel linkages which unfortunately it

has not been found possible to exhibit on the maps in such a way that they can be seen at a glance. There are clear indications that these are due in many cases to displacements of the known kind in one of the terms. In the maps the differences of the wave-numbers from the nearest lines before and after a given one are indicated. Although these are intended for a different purpose, they indicate such displacements by the frequent appearance of the same separations, and in many cases the same on both sides, e.g., in Ag, the mesh with one angle at 37233 (AgP i., j 7) is one striking example. Amongst such separations in Ag may be given as illustrations 52, 43, 37, 28, 16, where  $4\delta$  on  $p(-\Delta)$  is 52.16,  $3\delta$  on  $p(-\Delta)$  is 42.78,  $\delta$  on  $S(\Delta)$  is 36.15,  $2\delta$  on  $p(-\Delta)$  is 28.52,  $\delta$  on  $p(-3\Delta)$  is 16. But also 42 is the double link, c-b, and may indicate an unobserved line. As corresponding examples from Au may be taken the chain from 18449 (AuS (3). e. 12). A very exact example of lines at equal distances on either side is given by 26842 (AuX iii., d 14). The adjacent lines differ from it by  $-46^{\circ}49$ , and  $46^{\circ}49$  on either side. Now a displacement of  $2\delta_1$  on  $VX_{12}$  produces 46.44. They are therefore ordinary displacements  $\pm 2\delta_1$  on either side of 26842. A complete discussion of the whole spectrum must take account of these possibilities. The present paper only deals with the establishment of the truth of the linkages effect.

The majority of the linkages observed are represented in sixteen maps. method is in fact the only way in which the general connection can be visualised and realised. They are based on the differences as found and consequently must contain a considerable number of chance coincidences, although for the reason given above (p. 363) the number will be less than that given by the probability formula. In the present state of our knowledge there is little to decide where they occur. In a few cases the existence of a coincidence may be evident and be traced. For example, the lines 15923, 19113, in the AuX linkage which differ by 319013, or apparently by a modified  $\alpha$  link, really belong to a doublet of the D type, referred to in more detail later. They are respectively the  $D_{21}$  and  $D_{11}$  terms. The satellite  $D_{12}$  is 19738, which gives the normal separation 3815.54 with 15923. They are in inverse order—or their formula gives negative values. The satellite separation  $D_{12}-D_{11}=625.41$  and as it chances 3815.54 - 625.41 = 3190.13. Thus the apparent a link is not really so, it is a pure coincidence. It is further possible that links attached to these lines may reproduce other examples of this pseudo link. As a fact 15923 has a separation 17243 to 33165.51 and 19113 a link e = 17254.40 to 36367, which suggests a spurious link a = 3202.25 between 33165 and 36367.

In many cases it is easy to see that a spurious link must occur somewhere in a certain region. For instance, if a linkage starting from one series line runs on into that of another by a certain sequence of links, one at least in that sequence must be a chance coincidence. There are several cases of this, but astonishingly few when regard is had to the enormous number of links which exist. One chief difficulty in settling the true sequence in a case like this is due to the existence of the link

modification just considered. If only separations varying by one or two units from the calculated links are allowed, most of these difficulties, if not all, would disappear. In the maps in certain cases a suggested false link is placed in square brackets. The various cases are more definitely treated in the notes attached to each map as they occur. Another way in which the presence of spurious links is indicated is that of a complete cycle of links in which the links do not each cancel out with another of the same kind. Of true cycles, some examples have been given in Plate 6.

Another very long one is found in the map AuX, ii. and is considered on p. 388. Meshes also form a very numerous class of such small cycles. Of false cycles a few examples may here be cited for illustration from the general discussion below—

# (1) In the AgP linkage there occurs the cycle

This could only be a true linkage if  $s(-\Delta)+s-2s(\Delta)=2\{p(-3\Delta)-p(\Delta)\}$  which cannot be. The numerical values happen to be nearly equal in the case of Ag only. The link 2617 is not good, 3770-86 is practically exact and the 2460 belong to the long series (1) on p. 366. It is probable, therefore, that 3768.75 or 2617 is the false link in this case, most probably 2617.

## (2) In AgS (3) there is the mesh

where apparently 2c = b+d. This cannot hold exactly, but it must necessarily be approximately true for any metal, since by their constitution c must be near the mean of b and d. Clearly in this case 1004.42 is the difference 2c-b and is not a true link.

(3) Another similar but longer cycle occurs in AgD (4), which may be written

$$29084 + v - d + v + u + u + e - v + c - u - u + c - e - v - b = 29084.$$

In this case most of the links cancel and the set reduce to 2c-(b+d) as in the last case. The actual sequence can be followed on the map of AgD (4).

### THE LINKAGES.\*

It is found that, starting from any link belonging to the ordinarily recognised series, a series of other lines can be linked up to them in succession. These linkages are exhibited in a diagrammatic form in the maps appended. In these the wavenumbers increase towards the right. They are arranged in vertical columns for easy reference, the small p links stretch from one column to the next, the s links from one to the second from it, and the long e link over three. In this way the distance gives a general idea of the magnitude, and as a rule each column will contain wave-numbers of the same order of magnitude, although not always, especially when the links run forward and backward several times. The links are represented by straight lines, with the actual observed separations placed over them. Intensities are indicated by small figures over and to the left of each wave-number. These maps contain all the links noted to be related. In addition certain more abnormal ones, which other evidence, such as meshes or other regularity, render it advisable to put in evidence, are also shown. Also in many cases abnormal links are shown when they end a chain. In this case their presence can lead to no errors in succeeding lines. From these maps lists (pp. 391-410) are formed of some of the lines expressed as sums of multiples of the  $p(x\Delta)$ ,  $s(x\Delta)$  by considering them in succession with their links. explain themselves. The first column is an ordinal number for reference. chain ends the wave-number is printed in italics. In that case the next line will start a new chain branching from a previous line. The numbers attached in brackets to its ordinal number refer either back to a previous line from which it starts or forwards to the branching off of a fresh chain. Figures in brackets after a wavenumber give the small changes in it required to make the links correct, the last column of all headed  $d\lambda$  giving the corresponding O-C of wave-length. numbers in heavy type between the wave-numbers give the exact observed separations. The numbers in the columns under  $p(\Delta)$ , &c., give the multiples of these quantities on which the wave-number depends, and when the modified values with  $x\delta_1$  or  $x\delta$  enter, they are entered as (x). For instance under the column for  $p(-2\Delta)$ , 1+(-1) would mean in Ag,  $p(-2\Delta)+p(-\delta_1-2\Delta)$ . The columns headed s' or d' refer to the variable part of the series line from which the linkage starts. For example, in the S(3) linkage s' stands for VS(3).

#### I. Silver.

AgS (2).  $S_1(2) = 12082.63$ ,  $S_2(2) = 13003.42$ . Wave-lengths 8274.1, 7688.1 observed by Randall† in the ultra-red. The separation is 920.79 or 25 too large. If  $S_2$  is taken as correct, s' = VS(2) = 18561.61. Any single link attached to increase these values lands us in a region which has not been observed. If a linkage exists it is therefore necessary to try the sum of two links. It is found that there are two

<sup>\*</sup> This portion of the text should be read in combination with the respective maps (Plates 7 to 18) and formulæ tables (pp. 391-410).

<sup>† &#</sup>x27;Ann. d. Phys.,' 33, p. 742; 'Astro. Jour.,' XXXIV., p. 10.

lines, shown on the map, which are linked to  $S_2(2)$  by 3774.14 + 1007.23 and another by 2458+2416, clearly u+v, an enlarged e link is quite a common starting one from S and P series lines. Moreover the next link 959'49 is just as much displaced one way from c as 3774.14 is in the other from e, for 3774.14 + 959.49 = 4933.63 = 3771.00Thus the line 18744 28 is exactly e+d+c above  $S_2(2)$ . In fact we have a case of "series inequality." The link-966 09 to the next is excessive, but it is entered because (see list Nos. 3, 4, 5) the displacement  $(-\delta)$  in (3) is destroyed in (4) by adding a  $\delta$  to it, thus making it normal, and then another  $\delta$  on the (4) and on the -e link reproduces (5). So far all seems satisfactory but other considerations come in, in connection with the line 18744. There is an analogous set of doublets of the D type (see also p. 372) in each of Au, Ag and Cu with the proper doublet separation for each element. That they belong to the D type with negative values in Au and Cu is proved by their Zeeman effect, but the pattern for Ag has not been determined. The Au set show a satellite while Cu does not, as is usual with the first element in a group. In Ag the doublet set are  $D_{21} = -18026$ ,  $D_{12} = -18947$  with respective intensities of 4 and 1. There is a line 18756 also of intensity 4 which naturally seems to be  $-D_{11}$ , but its satellite difference is not sufficiently near a multiple of  $\delta_1$  to give confidence. The line 18744, however, which has just been suggested as belonging to the S(2) linkage with such good evidence, might just as well be taken for  $D_{11}$  were it not that its intensity 2 is less than that of  $D_{21}$  instead of equal to it or greater. On the other hand it makes the satellite difference exactly  $29\delta_1$  and so affords some evidence of its being  $D_{11}$ . There is also this in its favour, that both it and 18206 form a kind of combination with S(2) to give two lines in the ultra-red observed by RANDALL, whose wave-numbers are 5944'09 and 5740'40. How close this relation is can be seen from the following:—

$$18026.55 - 12082.63 = 5943.92$$
  $dn = .17$   
 $18744.28 - 13003.42 = 5740.86$   $dn = -.46$ .

At first sight RANDALL's ultra-red lines look like Ritz combinations but it is not so,\* since they should be written

$$D_{21} + S_1(2) = -5943.92 = p_2 + p_1 - VD_{12} - VS(2)$$
  

$$D_{11} + S_2(2) = -5740.86 = p_1 + p_2 - VD_{11} - VS(2)$$

\* All Randall's other ultra-red lines are, however, Ritz combinations, though his allocation would seem to be doubtful. For instance, using the notation employed throughout this series of papers, he gives  $5438.65 = VD_{11}(2) - VF(4)$ ,  $5460.66 = VD_{12} - VF(4)$ ,  $7965.33 = VD_{12}(2) - VF(5)$ . But if so the F sequence must be identical with the D series, as is clearly seen from the following:—

$$\begin{split} &D_{11}\left(2\right)-D_{12}\left(3\right) \ = \ 23730\cdot 99 - 18291\cdot 06 \ = \ 5439\cdot 93, \\ &D_{12}\left(2\right)-D_{12}\left(3\right) \ = \ 23730\cdot 99 - 18270\cdot 81 \ = \ 5460\cdot 18, \\ &D_{12}\left(2\right)-D_{12}\left(4\right) \ = \ 26232\cdot 50 - 18270\cdot 81 \ = \ 7961\cdot 69, \end{split}$$

in which  $D_{12}(4)$  is affected with a possible error  $\pm 3.7$  and 7965 of  $\pm 3.2$ . The equality of the F and D is pointed out by him. The lines considered in the text are given by him as  $VP_2(3) - VS(2)$  and  $VP_1(3) - VS(2)$ , but as the P(3) lines are not known it is not clear how he has obtained their values.

If, however, 18744 is really in the S (2) linkage, the second of the above would only be a coincidence, and 5740'86 would be a sum of links  $-p(\Delta)-p(-\Delta)+2p(-3\Delta)$  of which no other example is known. The existence of the two combinations together forms a strong argument that 18744 is the  $D_{11}$  line, and that the linkage relation is a coincidence.

AgS (3).  $S_1(3) = 21413.37$ ,  $S_2(3) = 22333.79$ , s' = VS(3) = 9231.23. In the map of this linkage there must be at least one spurious link shown by a complete false cycle, and two possible ones shown by two chains, one leading to D(5) and the other to P(1).

The links from the S(3) mesh back to 17874 (No. 6) are all good except the two successive 2613.74 and 882.58. They are admitted, however, because they are an example of series inequality deviating by the same amount (1.7) in opposite directions from exact normality. They clearly point to a displaced  $u(\delta)$  link for the first with the displacement annulled in the second. With the long e links stretching from S(3) to 28968 we get the enlarged values which seem frequently to be associated with the chief lines.

From 28968 two chains diverge, one through 31429 ultimately leading to D(5) through 30393. There are no clear indications to show where the false link occurs. The first link  $u = 2461^{\circ}12$  is so large that at first sight it might seem to be spurious; but it falls in well with the others as may be seen from the formula list. It would look as if the series of long links should be 3773.59, 3778.77, 3778.77, i.e.,  $u(-\delta)$ ,  $u(-3\delta)$ ,  $u(-3\delta)$ , but that the last for some reason took  $u(-2\delta)$  at first but completed the extra  $(-\delta)$  in the next link. The formulæ in this chain, as will be seen, involve very few displaced links beyond those it started with, due to the above indubitably enlarged e links. In fact such only enter in No. 21 and in 25, 26, which latter form part of a mesh. On the other hand, as will be seen below, the formulæ based on D(5) show very good links up to 29514 and even beyond. Provisionally I have placed the spurious link as that between 29514 and 30394 with  $\alpha = 878.72$  in place of 880.77.

Returning to 28968 and considering the other branch chain from it, the second link 918'65 is small, but is naturally accounted for by the long e—which entered as due to 3779 after  $S_1(3)$ —changing to the same value as the second e link 3776 which entered immediately after it. The links 2455'51 and - 2461'79 appear at first sight too abnormal, they are exactly explained by a return of the two long links after  $S_1(3)$ , which became equal in No. 27 to the value of that before  $S_1(3)$ . From 30806 starts the false cycle referred to above. In order to keep the map as open as possible the line appears in two places in it—here and at the top of the same column. In the absence of sufficient knowledge of the laws governing links it seems impossible to point out where the pseudo link occurs. The long links 3774, 3778 which usually appear successively here appear separated by -b+c, although a set b+c appear as if a part of a missing 3778. This consideration would therefore favour

-921.42+963.80+3778 (see map) as real. Again the succession of links through 30806 of 3778 - 919.58 + 963.91 - 919.78 + 959.69 would appear to signify a real succession. There would then remain the two u links  $-2456^{\circ}66$  and  $-2457^{\circ}69$ . To make the latter correct 29358 should be 1'49 less. This would bring 921 and 3774 nearer their normal values, but would make 920.75 too large. On the other hand 2456 is about a  $\delta$  displacement on u. Provisionally, therefore, the false link is located between 29358 and 31815. The evidence for this allocation is not strong, but it is strengthened somewhat from the formulæ. These show (No. 41) that the two e links introduced after  $S_1(3)$  are now cut out by the others, pointing to their being parallel sequences. Further the set of modified p links stretching from 30806 produce in the end a change  $-2p+4p(-\Delta)-2p(-2\Delta)$  or 2(b-c) in which all modification has disappeared. Nos. 41, 42, and 43 afford an example of series inequality. The odd links attached as tags to the lines here considered fall naturally into the formulæ. Those given for Nos. 46 and 49 depend directly on the formulæ for the lines to which they are attached. They can, however, take the simpler alternative forms given if displacements are allowed in the other terms. The line 29803 (No. 35) is 3777.54 ahead of  $S_2(4)$ , so that it might possibly be the commencing line of a S(4) linkage, in analogy with all the other lines. But the line falls in so naturally in its present position that the connection with S(4) is possibly accidental (but see below under S(4, 5)). From 33179 (No. 37) a side chain starts which apparently leads into the P linkage. As will be seen below when the P linkages are considered, the links up to 33179 seem 33179 would seem a good S(3) line and possibly one of the p links near it may be spurious, viz., 961'23 or 960'83, or again 2456'66. The difficulty must at present be left open.

AgS(4).  $S_1(4) = 25106.89$ ,  $S_2(4) = 26025.60$ .

The only apparent link from these is that referred to in the foregoing, viz., 3777.54 from  $S_2(4)$ .  $S_2(4)$  is not a good observation (possible error = 13.5). If it be corrected from  $S_1(4)$ , which is much better (.9) by adding 920.44, the link becomes 3775.81, which is  $e(-2\delta)$ -31, and 31 gives  $d\lambda = 03$ . It is thus so close to the usual link which starts from the series lines as to make it very probable that it is a real link. If so, other lines from those allocated above to S(3) will probably be linked up, and another spurious link will exist amongst the S(3) set.

From  $S_1(5)$  a link 3776.76,  $e(-2\delta)+58$  goes to 30722, which occurs also in the S(3) linkage next to that related to  $S_2(4)$  to which it is connected by a link 919.58. Now  $S_1(5)-S_2(4)$  is 920.36 or an exact b link, the exactness of which, owing to the uncertainties of the measurements, must be pure chance. If  $S_2$  be corrected as above, the difference would be 918.63, still within limits of  $S_1(5)$ . There is then formed a mesh:—

$$S_{2}(4)$$
 26025 3777·54 29803 920·36 919·58 (?)  $S_{1}(5)$  26945 3776·76 30722 3 G

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The conclusion to be drawn is that 26945 has been wrongly allocated to  $S_1(5)$  by Kayser and Runge. It is further in favour of this that the difficulty as to the different limits for the S and D series referred to in [Part III. p. 404] is got rid of. The link 919.58 above comes in in the cycle from 30806 in which a number of doubtful links must occur. This one is clearly real, and it suggests that the adjoining one on the map for S(3), 963 is a false one. The lines 27140, 28103 would then come into the S(4) system. The map for S(4) has been drawn thus:

AgP (1). 
$$P_1(1) = 30471.73$$
,  $P_2(1) = 29551.26$ ,  $VP_1 = 30644.66$ ,  $VP_2 = 31565.10$ .

The linkage stretching from  $P_2(1)$  is by far the largest, over 280 lines appearing as linked together. In many regions the linkage is so complicated that it seems impossible to exhibit it in one map. Four maps are used to show the connections, a chain leaving a map at one line and passing on to the same line on another map. Amongst such a large number there must be many coincidences, and in fact the presence of some of them is shown by cycles in which the links do not identically annul one another. There are also a few cases of chains which appear to pass on to other independent linkages. It will be necessary, therefore, at first to make an attempt to clear up these ambiguities.

The following cycles occur:—

1. 37574-43720. In map (i.) there is a chain from 37574 (col. k) to 43720 (col. p) with links:—

$$-b+c+c-u-v+e-b+e+c+v = -2b+3c+2e-u.$$

In map (ii.) the same lines (col. i to col. n) are connected by the chain

$$-e+b+u+v+v-e+u = b-2e+2u+3v$$

If these are supposed all normal, their sum would be 6130.31 in (i.) and 6145.55 in Now  $43720\cdot43 - 37574\cdot77 = 6145\cdot66$ . Although not an absolute proof, this exact agreement with the total links in (ii.) is almost convincing that the pseudo link lies somewhere in the chain in (i.). But the links in (i.) are most of them good modified links. Thus going back from 43720 (see map (i.))  $2619.25 = v(-\delta) + 19$ ,  $963.75 = c(-2\delta) - 19$ ,  $3776.44 = e(-2\delta) + 26$ , 921.01 = b + 54. The 54 is partly due to error '26 in the previous and a further - '28 on the line 37282, which makes all the neighbouring links better. 3775.55 is  $e(-2\delta)-68$  or  $e(-\delta)+1.9$ . 1.96 is large, but if 33506 is 1.96 less ( $d\lambda = .17$ ) all the other links converging on it become normal, viz., e, v. The link  $2456^{\circ}44$  is  $u(\delta) + 05$ . The next link  $964^{\circ}80$  is larger than the It is  $c(-3\delta)$ + 28. We might be doubtful about this were it not that the next is  $960.08 = c(3\delta)$  - 48 and their sum 2c - 20 or two normal c links (example of series inequality). The last is  $921.78 = b(-2\delta) + 12$ . They all, therefore, apparently fit in well. The  $\delta$  displacement in the  $\rho$  links is, however, so small that little weight can be given to their agreement. Now a glance at the probability curves (Plate 4) shows that 921.75 and 964 occur with frequencies less even than the calculated chance

probability. The spurious link is therefore probably one of these. But if the 921.75 link is retained there is a sequence through 37574 of e and b links e+e-b+e-b+e, the regularity of which would seem to have a reason, and would include 921 as real. Provisionally, therefore, 960.08 or 964.80 (or both) is taken as spurious.

- 2. 38577 in (ii. j) to same line in (i. l). There are two cycles in this case. In one the complete cycle of links is, starting from (ii.), d+v-c+e-v+u-c+u-c-v+e (43720 (ii. n) pass to (i. p)) -v-c-e+b-e+v+u=b-3c+d-e+3u-v. In this the second c link is 96671. It is so excessive that it should scarcely have been included. We shall probably be right in rejecting it. The other is, starting from (ii.), d+v (pass to (iii. m)) +c-e+c-u-u-b (pass to (i.)) -d+v+u=-b+2c-e-u+2v. Provisionally, the b link 922.51 may be marked as spurious.
- 3. The cancelling of the link 966 in the preceding case also annuls two other cycles, one a long one from 35435 in (ii. g) to 42203, thence to (iii.), and the other from 35435 through 33506.
- 4. 29737 appears both in (i. e) and (iii. c). The cycle is annulled by omitting the large  $u \lim 2462.70$  in (ii.) after 35150. The linkage connected, however, with 29737 probably belongs to D (4) to be considered immediately.
- 5. 29084 on (ii.) is connected across to 31703 by a link v = 2619, the latter line belonging to 29737 just considered. The cycle is annulled by omitting the abnormal link 958.25 after 35435.
  - 6. There is also the case given as an example on (p. 373) and there considered.

With the links indicated above left out, the P linkage is now singly connected, except in the case of true cycles. There remains, however, one chain which leads on to the D(4) linkage. The line 29084, appearing in the cycle (5) just considered, is itself a part of the D(4) system. It is linked to  $D_{12}(4)$  and  $D_{11}(4)$  by a mesh, and it is practically certain that this connection is real. In this case a certain set of lines attributed to the P linkage must really belong to D and a false link must occur. 29084 is joined to 31703 by 2619.80 =  $r(-\delta)+74$ . It is impossible to notice the sequences of this link with the p links on the left hand top corner of (iii.) without being convinced that they form a connected cluster. It is difficult, however, to see where the false link comes anywhere on the chain up to 42203 which is connected in several ways with P lines, or at least with lines attributed to P. Further discussion is deferred until the D(4) linkage is considered.

With the lines in the map now singly connected it will be possible to write down their formulæ in terms of the p and s values. As, however, in such a large number of lines there must still remain a number of spurious links, and as the existence of one of these will invalidate all the formulæ for lines occurring later, only the first sets starting from  $P_1$  and  $P_2$  are given here. From  $P_1$  a single chain stretches which is remarkable for the long series of enlarged e links. They are all close to their mean  $3778^{\circ}44$ , which only differs from  $e(-3\delta)$  by 33, and at the same time the link to  $P_1$  is  $u(\delta) + 25$ . This chain, therefore, appears to support the theory of link

displacements adopted for the purpose of indicating their modified values. formulæ given in the AgP<sub>1</sub> list agree very closely with the observed values and depend, as is seen, on  $(-3\delta)$  displacements of e and  $\delta$  displacements in u and v. In the AgP<sub>2</sub> list our displacement convention has been departed from in No. 13 and dependent lines by assuming a displacement  $3\delta_1$  in  $p(-2\Delta)$ . This makes the link 3777 cut out a former e link and reduces the formula to two terms. far as it can be from an e link displacement, and the suggested formula only gives a  $d\lambda = -0.07$  error. From 28600 a long v link 2621.11 =  $v(-2\delta)$  - 40 connects to the whole succeeding P<sub>2</sub> lines through 31221. Some doubt might be felt as to its reality, but it is accompanied by an enlarged  $u \text{ link} = u(-\delta) + 15$ , which suggests a parallel The formula for 31221 gives  $d\lambda = -02$ . It may be simplified to  $s(-\Delta)$  $-p(-2\Delta)(\delta)$ , giving  $d\lambda = -13$  possibly within observation limits. But if so, the error dn is such that it entirely upsets the parallel inequalities in the succeeding mesh. It is, therefore, not adopted, although the line 30214 has the analogous form  $s(-\Delta)-p$ Further, this error makes the parallel link 2461'04 into  $(-3\Delta)$  ( $\delta$ ) with  $d\lambda = -12$ . 2459.62, i.e., would replace  $u(-\delta)$ -.05 by one as far as possible from a displacement value.

The double mesh from 31221 is noticeable for the great modification in the links. They are, however, examples of parallel inequality which demand with each link some displacement continued for each case. In the table it is supposed to be  $(-3\delta)$  on the b link. It is possibly, however,  $(\delta_1)$  on the p  $(-2\Delta)$  term. From 30415 the list passes from (i.) to (iv.) and is continued to the strong line 34446.

The D linkages. I have not been able to find any links attached to D(2) or D(3). They exist, however, for D(4) and D(5).

 $D_{11}(4) = 26235.29$ ,  $D_{21}(4) = 27153.03$ ,  $VD_{1} = 4409.31$ ,  $VD_{2} = 4412.01$ , giving satellite difference 2.70, but the measures are not very accurate, especially that of D<sub>1</sub>. There is a considerable linkage in which no cycles appear. It contains, however, the line 29084, referred to under the Plinkage, as connecting with lines in it. is itself a clear D line, as the linked mesh in the map shows. In order to test the links into the P map lines, the formulæ have been calculated up to the strong line 38234 (see AgP (iii.)). The modifications of many links would seem to point to displacements producing about 1.5. For instance in the first eleven links there are three examples, viz., the links below Nos. 1, 4, and 9. It is possible that they occur in the d sequence and not in the links themselves. For this reason and because the actual D (4) lines may be considerably in error, displacements have not been introduced into the formulæ, and errors up to  $d\lambda = 1$  or 2 have been admitted, whilst changes from the satellite sequence  $d_2$  to the chief line sequence  $d_1$  have been allowed. But as a fact there does not seem to be much demand for these displacements either in D(4) or D(5), and the linkages are distinguished from those for the P and S linkages by their absence. In No. 2 there is an example of a link acting as a pure displacement so that the three lines  $(\Delta)$  D (4), D (4),  $(-\Delta)$  D (4) exist. The link after No. 6 has been taken as normal, although its amount is  $v(-\delta)+21$ , on account of the large errors required in 5, 6 caused by neglect of the apparent displacement 1.5 in the fourth link. The e link between Nos. 18, 19 might be the usual modified  $e(-2\delta)$ , but the arrangement adopted to change from the satellite  $d_2$  to the main  $d_1$  would seem preferable. A change from  $d_2$  to  $d_1$  also comes in Nos. 24, 27. It is curious to note that all the chains terminate with changes near the end from  $d_2$  to  $d_1$ , with the exception of those ending at 32062, 35044, and the doubtfully linked 32936.

From No. 38 begins the chain which runs into the P map through some false link. The formulæ are written down as far as the strong line 38234, and so far all the links fall in very naturally and give small  $d\lambda$  values. The false link is probably, therefore, beyond 38234. This last may be written wholly without displacement, those in u, v disappearing in it. The list is then continued to embrace the other lines belonging to this chain. It is interesting to see how the links fall in naturally, with the possible exception of No. 50, which may be a coincidence.

AgD (5). The only D (5) line observed is  $D_{11}(5) = 27586^{\circ}13$ , but with the large possible error of 3.8. It differs, however, from the value as calculated from the series formula by 1.67. If it be taken as about correct with a small satellite difference the values of  $D_{12}$  and  $D_{21}$  would be about 27585.33 and 28505.77. From these approximate values it will be seen that linkages extend as shown in the map. The table of formulæ for the lines are practically all normal links with small errors. It will be noticed that No. 7 continues the succession of  $D_{12}$ ,  $(-\Delta)D_{12}$ , by  $(-2\Delta)D_{12}$ . The case of 29514, No. 3, as connected with the S (3) linkage, has been there considered, and it was suggested that the false link was at 878.72. The table gives the formulæ for a few lines placed in the S (3) linkage on the supposition that it is a real link. It is seen how simply the formulæ come in, but it is only possible owing to the large error which had been attached to 29514, and this again has been caused by the adopted value for  $D_{21}(5)$ . The formulæ in S (3) appear more complicated because of the abnormal e links; the changes in each table from line to line are of course the same.

### II. Gold.

In the case of gold the series lines in the arc are few, and even these are not certain, with the possible exception of the two P(1) lines, They are considered in [III., p. 404], and the way in which the constants there determined reproduce the links found in the spark spectrum affords very strong confirmation of the methods there employed. The methods are based on an identification of the  $D_{12}(2)$ ,  $D_{11}(2)$ ,  $D_{21}(2)$  lines. These, therefore, will be taken for granted now. I suggest, but with no feeling of certainty, two lines for  $S_1(3)$ ,  $S_2(3)$ . Their position and their calculated denominators show that they range well with those of Cu and Ag, but there is no further evidence beyond their doublet separation. They, however, form starting points for long linkages which provisionally may be called by their names. The gold linkages

are many of them very long, and naturally the presence of mere coincidences with link values is to be expected to a greater extent than in silver. The result is that in many cases a chain will appear to run from one linkage to another. No attempt, however, has been made to locate the spurious links, as such identifications would be even more uncertain than in silver. It will be sufficient to indicate where a chain runs on from one map linkage to another.

$$\text{AuS}(3) \cdot \text{S}_1(3) = 20776.50, \, \text{S}_2(3) = 24592.07, \, s' = \text{VS}(3) = 8688.68.$$

At the first glance the presence of a large number of meshes involving the long e links is noticeable. In the notes to the maps it will be advisable to follow the lists so far as the formulæ are written down. The residual differences between the observed and calculated values might in many cases be reduced by admitting displacements, but it has been thought better in the present state of knowledge to seek for simplicity of a first approximation than exactness where the observation errors are quite unknown.

The separation of  $S_1$ ,  $S_2$  is practically exact. There seem to be several links about 3188, which have been introduced on the evidence of meshes. From  $S_2(3)$  3199 is regarded as  $3198.54 = a(-2\delta_1)$  and the next a link as  $3188.34 = a(\delta)$ , but the two together can be regarded as  $2a(\delta_1)$  in the value for 22813 and succeeding lines. the 3199 and the 3191 from  $S_2(3)$  form a good example of series inequality, their sum being practically an exact 2a. The successive links 11347 and 14931 No. 7 would not have been admitted singly, but the excess of the first and equal deficit of the second point to a displacement in 28525 which does not recur in the preceding and succeeding It may be noticed that the order of operations is  $S_1$  to  $S_2$  by a displacement  $-\Delta$ in the limit, then a modified -a link, then by another  $-\Delta$  displacement, again by a modified -a link. In the list as originally drawn there was no further  $-\Delta$  displacement which should be 5635 ahead. But there is a line 28439 which is 5626'92 ahead. This is just as much in deficit from a d link as the previous 3188 from a. It is therefore a d link with 3188 made normal, and clearly comes naturally into the system. This again has a modified -a link. If the law continued an extra  $-\Delta$  displacement in the limit would give a line 6993 ahead, but none is found. It would correspond to a  $p(-4\Delta)$  term. The sequence is also continued back to 23966 by a modified  $\alpha$ Thus from 20768 we have the sequence and thence by  $\Delta$  displacement to 20768.

$$20768 = p (\Delta) + X (say),$$

$$23966 = p + X,$$

$$20776 = p - a (2\delta_1) + X,$$

$$24592 = p (-\Delta) - a (2\delta_1) + X,$$

$$21392 = p (-\Delta) - a (2\delta_1) - a (-2\delta_1) + X = p (-\Delta) - 2a + X,$$

$$26000 = p (-2\Delta) - 2a + X,$$

$$22813 = p (-2\Delta) - 2a - a (\delta) + X,$$

$$28439 = p (-3\Delta) - 3a + X,$$

$$25249 = p (-3\Delta) - 3a - a (\delta) + X = p (-3\Delta) - 4a (\delta_1) + X.$$

As supporting the theory of displaced links, the mesh at 26000 (c 12 and No. 4) is interesting. For the link 17256 is easily explained by the displacement in a disappearing, and the link 17250 by its continuance to the line 22813. In fact the sum of the two links is 2e-24. From 26000 the link 14929 is not entered as it is so small, but there are other examples of this small v in this map and the c link appears to be a normal associate with an e mesh.

Starting from  $S_1$  there are four separations close to 17264 or  $e(-\delta_1)$ . The link 4611'32 is too much out to be introduced on its own account, but it forms part of a mesh whose corresponding link is evidently c. It is taken as  $c(-\delta_1) = 4610^{\circ}52$ . A displacement somewhere in 42644 producing 3.51 not only makes the long link e correct, but with the disappearance of the  $-\delta_1$  displacement on the preceding c at the same time makes the separation to 26698 a correct u link. The alternative formula (No. 15) is on the supposition that the displacement is produced in the e by  $2\delta_1$ . Perhaps we should stop at 33345 as the next link 14929, like the one referred to above, is 7.70 too small. But the next e link is too small for  $e(-\delta_1)$  by about the same amount, and the two together have the appearance of a parallel inequality. The abnormality however may possibly be due to the fact that the separations are due to differences between one line by EDER and VALENTA and others by EXNER and HASCHEK. If this be granted the next comes right with  $e(-\delta_1) = 17264.03$  with error  $d\lambda = .07$ .

Again starting from S<sub>2</sub> there is a collection of meshes, chiefly of e. They illustrate the variations from normal links chiefly in link a. A noticeable peculiarity is that in most of these meshes a line is linked by v to one corner, in all cases v being from 3 to 4 below its normal value. The regular presence of one of these links in each mesh would seem to exclude any explanation as a chance grouping. But they further exemplify the theory of displaced links in  $a, b \dots$ , for the defect from the normal values of v is not due to themselves but to a concomitant return of a displaced  $\alpha$  or b to a former value. Thus in 26130 c recurs to its value in 23805. The line 39404 apparently linked to 45043 by  $-d(-\delta_1)$  really takes the -d link, and the displacements in 45043 are annulled. Also 50676 wipes out the same displacements and is 2d above 39404. The line 26130 is of intensity 8. If the general rule that the strongest lines are connected with an e link is satisfied there should be a mesh with a line at 8866, which is outside observed limits. The lines on this hexagonal mesh (Nos. 25 to 28) appear also in the Y map. From 31921 we get a series of enlarged p links with similar displacements ending at 24912 (No. 38) with all the previous displacements annulled. In 39404 above there is a similar example of the chain stopping when the displacements cut out.

From 25387 (c 3) the chain passes to a separate map to escape excessive crowding. In the next two lines we get two repeated  $\delta_1$  displacements in c links which return to normality in the third. The line 58271 is from Handke's ultra-violet lines and is affected with considerable possible observation error. The formulæ are continued

from this, but with increasing doubt as to spurious links. In fact the long succession of p links in series in the lower part would seem to point to connection with a diffuse linkage. The presence of such a spurious link is shown directly also by the appearance of the line 27783 in two places, cols. d and g indicating a cycle.

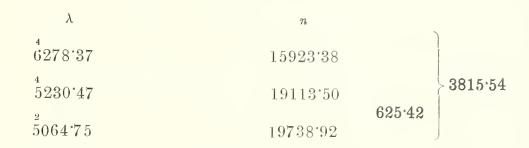
AuP.  $P_1(1) = 41172.94$ ,  $P_2(1) = 37357.62$ ,  $P(\infty) = 70638.12$ . The linkage as shown in the map is much smaller than in the case of Ag. This is doubtless due to the fact that in both cases the chains start with the long series of e links. In Ag several of these in succession lead up to the ultra-violet region from which chains run back again towards longer wave-lengths. In the case of Au, however, two of these long e links carry right across the observed region, and if the Au linkage is analogous to that of Ag, the points from which linkages would run back again are beyond the observed. Possibly some may exist amongst Hander's ultra-violet, but the observed possible errors in n are so excessive, due to the very large multiple of  $d\lambda$  as well as to large possible values of  $d\lambda$ , that it is best to neglect them. There are several links in the neighbourhood of 17260, where  $e(-\delta_1) = 17264.03$ , and of 17258. It is possible these may be e links modified in some way not yet known. In the lists, however, the attempt has been made to explain all these modifications by displacements on the links in general.

Starting from  $P_2(1)$ , if the first link is e without any modification, there must be an error  $d\lambda = 7$  in the line 20100 which is hardly credible. If, however,  $p(\Delta)$  and  $p(-\Delta)$  in the formula have displacements  $-\delta_1$ , the error in this line is reduced to  $d\lambda = -25$ . The line 60270 is from Handre. As the  $dn = 36 d\lambda$ , it is just possible that the link from it to the previous line might be a normal e or  $e(-\delta_1)$  link. The link 11332'4 from 54617 is about 10 in deficit and may be spurious, and in fact it leads on into the X linkage. It is, however,  $u(\delta_1)+62$ , but this and those beyond have been excluded from the list. In support of this further evidence is available from the consideration of the  $D_2$  linkage below. A mesh with clear  $e(-\delta_1)$  links is based on  $P_1(1)$  and  $P_2(1)$ . The formulæ seem to run naturally down to 18432, which as in several cases ends the chain by annulling all the displacements. From 34669 a chain leads to the AuX map. It would seem impossible at present to determine where the spurious link comes. It may be noted that whilst 34669 contains  $-e+e(-\delta_1)$  there are lines on either side linked by +e and  $-e(-\delta_1)$ .

The curious double mesh attached to 40305 contains very abnormal links, but with the calculated error — 8 which the formula gives to 40305, the links from it form two pairs of parallel inequalities, viz., 11345'92 and 14933'8, which deviate equally in opposite directions from their normal values. The lines are probably really connected.

The D Linkages. In [HI] the lines allotted to D(2) are  $D_{11}(2) = 17125$ ,  $D_{21}(2) = 20858$  with the satellite too faint to be observed, but giving a satellite separation of 82.11. Linkages start from both these lines. In addition there are the three lines of a D type corresponding to similar ones in Cu and Ag already referred to (p. 372).

They are



The Zeeman patterns of two have been observed by Hartmann. His measures, though not perhaps very exact, seem to fit in with the D type, the Zeeman patterns of the first two being represented in the notation suggested by me\* by 0/5 and  $0/6\frac{1}{2}$ respectively. These are the patterns for  $D_{21}$  and  $D_{11}$ , so that the set are in the reverse order to the usual one, and the relative intensities agree with this. This means that calculated as first lines in a D series they have negative values as is the case when the first P line is calculated from the S formula. If the limit be taken to be the same as for the diffuse, in agreement with its normal separation of 3815.54, the denominator of the  $VD_2$  becomes 1'492977 with a mantissa about '5 below that of  $D_{11}(2)$ . The satellite separation of 625.42 is produced by a satellite difference in the denominators of  $27 \delta_1$ . Starting from these, a linkage of very great length extends, requiring five maps to represent them. But it also contains the  $D_{11}(2)$  and  $D_{21}(2)$  lines, has connections with other linkages as well as possesses a certain number of false cycles. There must therefore be many spurious links. No attempt is made to locate them fully as was done in the case of silver, partly because they are more numerous and also because the greater difference between modified and normal links renders the entrance of spurious values more easy and their detection more uncertain. The whole linkage is given in a set of five maps in which the line at which a chain leaves one map or appears at As the origin of the set is not certain it is represented by the another is indicated. letter X.

The satellite difference of the three lines forming the starting point is 625.42. Now there are a large number of lines with a difference of about 600 which look as if related to this in the same way as the F separations depend on the D satellite. It is too small to be in analogy with the general case of F series in elements of other groups, but a similar diminution is apparent in Cu and Ag. Many of the lines showing this difference are connected to v links in a peculiar way. In several cases lines  $n_1$ ,  $n_2$  differing by 600 have a line at  $n_1+v$ ,  $n_1$  being weaker than  $n_2$  and looking like a satellite. The difference between  $n_2$  and  $n_1+v$  is 14337. Now there are a very large number of pairs of lines with this difference, indicating apparently the existence of fainter satellites (the  $n_1+v$ ) not observed. Where such a difference occurs with a line in any of the maps it is indicated by a short broken line—to the right when added and to the left when deducted. As one example of the difference 600,

a map Y is given starting from 18069 which is 599'41 behind 18668 in Au X. i., and is also attached to a typical v link. No formulæ, however, from this map have been discussed.

In the map X. i. appears a congery of meshes, two of which seem to afford some support for the suggestion as to the connection between 600 and 625. The meshes in question may be represented as follows:—

22253	11342.36	33595
14934.77		14935.17
37188	11342.76	48530
-14914.64		-14911.43
22273	11345.79	33619

The value 14911 would never have have been admitted were it not for the evidence of the numerous u, v meshes in this region. Their values may be explained as follows. The line 33595 depends on the  $d_{12}$  (i.e., the  $X_{12}$ ) sequence. The line 33619 is 23.74 greater, and this is the value of a  $\delta_1$  displacement on the  $d_{12}$  term. If  $d_1$  remains unchanged, and the  $D_{12}$ ,  $D_{21}$  (i.e., the lines depending on  $d_{12}$ ) are thus displaced, the satellite separation  $d_{12}-d_{11}$  becomes 23.74 less, i.e., about 601. In this case the 14911 are not modified links, but are normal v links with a simultaneous displacement on the  $d_{12}$  or  $VD_2$ . The F type separation of 600 is produced by the new  $d_{12}$  and the unchanged  $d_{11}$ .

A very common difference found in the Au spectrum is 1000. Where it enters an arrow is attached to the number representing the line, to indicate its existence. If D(2) be the first diffuse line,  $VD_{11}(2) = D(\infty) - D_{11}(2) = 12340 = F_1(\infty)$ , the limit of one of the F series. It is noticeable that  $F_1(-\Delta) - F_1 = 1000^{\circ}4$ . The 1000 is therefore a link based on the diffuse sequences, the consideration of which has been excluded from the present paper. There are also a very large number of separations equal to that of the D(2) satellites, viz., 82.

It will be instructive to write down the formulæ for short regions of the X maps, but no useful purpose would be served by attempting to do this throughout. Starting from the  $X_{21}$  line 15923 in AuX. ii., we find the long series of d links already referred to (No. 4 on p. 366). It is noticeable that the last three sum to 16905.87 =  $3 \times 5635.29$  or three exact d links. At 38457 the chain passes to AuX. iii., and 38457 is a starting point for the very remarkable congeries of meshes already referred to (fig. c, Plate 6). The formulæ for only one of these is written down, but all the e links cluster round 17257, and it looks as if they are sums of single displaced p links. The link 4612.68 from 21201 (No. 8) has only been admitted on account of the mesh. It also comes naturally from the formulæ for 21201 by annulling displacements, viz., in the 3rd and 4th columns of the formulæ tables from  $-(2\delta_1)$ ,  $3-(-\delta_1)$  to -2,  $-4+(-\delta_1)$ . At 38457 also a chain links on to  $D_{21}(2)$  by a b link = 3813.78. This link, however, is one of three

in series 3815'40, 3813'78, 3812'74, the last in a mesh. They are probably real. The next link, 11341'38, is clearly a true u link. Of the two next+3192'59-5635'63 to  $D_{21}(2)$  the second is a very close d, and it would appear, therefore, that the spurious link is 3192'59, which is about as far as possible from a modified a link. There is also a long chain stretching from 21558 in map (ii. b. 4) to  $D_{11}$ , which will be considered later.

The linkage is now taken up from 21558 (i. b. 3) with a chain of a large number of links requiring few modifications. Nos. 14, 15, 16, are parts of two meshes, equivalent to parallel sets of three lines at a distance 3197.7. The second mesh is the case taken as an example on p. 367 to illustrate the reality of displacements. The opposite sides of the mesh are exactly equal, so that it is highly improbable that errors of observation enter to any extent. The values of the four  $\alpha$  links are as far as possible from modified ones, and the displacements must arise in some other way, the lines 41325, 41320 being displaced in opposite directions from 41322.74. formula is given for this and the two displacements entered under  $d\lambda$ . There is an analogous mesh at the bottom of col. f attached to 25813, but involving two different links. The sides 3199.19 + 4603.92 = 7803.12 whilst a+c = 7802.91. This region is a maze of links which have a look of reality, even modified links constantly repeat themselves in similar arrangements, for instance 11345, 14935, 17250. The formulæ are continued from 38127 (i. e. 6) by a chain through them from which the formulæ for the other lines can be easily written down. The chain from 18985 (i. f. 1) in the annexe is parallel to one from 18577 (i. a. 1). From the  $X_{11}$  line, 19113, only a short chain extends with a problematical link at the end. It depends of course on  $d'_1$  instead of  $d'_2$ .

At No. 25 the X<sub>12</sub> satellite is taken up. At 17410 on the diagram the chain passes from (a. 3) to (f. 2) for convenience of spacing. The part from 17410 to 41866 appears also in the P map, and the P formulæ for 17410, 28755 are Nos. 20, 21. In this chain it should be noted that a line—an enhanced one—is connected to 36991 by a link 11345.09. The Zeeman pattern, as found from Hartmann's measures, is  $0/6\frac{1}{2}$ , viz., that of a  $D_{11}$  line. It is connected by the links e-u to a  $D_{12}$  line for which the typical pattern is 5/10. This relationship is certainly not to be expected, and throws some doubt on the link 11345'09. Formulæ are given as far as 18985. representation of the slightly abnormal u, v links looks artificial. The abnormality is clearly real, as they so frequently appear and in similar positions. It is possible they are due to displacements in the VD with a kind of satellite displacement, but if so they are too small to be accounted for by  $\delta_1$  displacements. From 19738 another chain starts—drawn in the lower part of the map—containing again a number of the same abnormal u, v links. Nos. 25, 26, which are separated by a very exact e link, have the equal abnormal links attached symmetrically, viz., 11345.52 to No. 25 and -11345.09 to No. 26. The symmetry is striking, but the first leads to a connection with the S(3) linkage and the second is that on which the Zeeman effect has thrown

doubt. The formulæ for this chain have not been written down, partly because of the prevalence of the small modified u, v links, and also because a few false cycles show that some spurious links occur. In the X. i. map we have an example of a true cycle from 23354 (c. 11), viz., a+d-a+c-d-c=0.

AuD (2). AuD<sub>11</sub> (2) = 17125.54, AuD<sub>21</sub> (2) = 20858.97, VD<sub>1</sub> = 12339.64, VD<sub>2</sub> = 12421.75. The linkages appear amongst the X maps.

The line  $D_{11}(2)$  appears in the X. ii. map in col. a. From this a chain proceeds to the top of the map consisting, like other D linkages, largely of p links. They fit in well and the formulæ are simple. Another chain extends downwards into lines which at first sight appear analogous to those in X. i. There is, however, a remarkable long cycle which rather seems to indicate that the majority of the lines in X. ii. belong to the D(2) series. The line 28620 appears at the top of the map at (e. 2) and also at the bottom, shown in the inset map at (i. 4). A true cycle runs between. Starting from (i. 4), and supposing all the links normal, they run in the following order to (e. 2) d+u-a+c-b-u-d+a+v-e+v-c+d-v-a-c+b+a-d+c+e-v in which each kind of link is annulled. Although not an absolute proof it produces conviction that all the links are real. The whole series forms, so to say, the backbone of the whole map in which only the side out-liers may be doubtful. Assuming this it is easy to suggest the position of certain spurious links. For instance:—

- (a) The chain from the true  $X_{21}$  line (15923) joins this cycle at the line 42016 (f. 7) by the link 3197.66. This joins the corner of a mesh which is undoubtedly an  $X_{21}$  set. This link is probably spurious and is marked doubtful. It differs as much as possible from a displaced  $\alpha$  link.
- (b) From 26303 (d. 3) a connection passes to the P map. It is the case already referred to in the discussion of that linkage. The connection must be spurious, and the false link is probably the 11332 on which doubt was there cast.
- (c) A long cycle also stretches from 24273 (g. 2) to (i. 8), but this is a false one. It only has one link in common with the other, viz., that connecting 42397 and 47004—(g. 13) to (h. 9).

 $D_{21}(2)$  appears in AuX. iii. b. From it a chain runs down to 38457 which has been taken to be on an X chain. The links, however, all seem good from the present point of view. If the  $D_{21}(2)$  and X lines are correctly allocated there must be a spurious link here. If the links are real then  $D_{21}(2)$  and X are not independent, and one at least has been incorrectly allocated. It is at least interesting to notice that the formula for 38457 depending on  $D_{21}(2)$  involves no displacements and reproduces the observed value by  $d\lambda = -0.05$ . From 26494 another chain is drawn upwards. The formulae are written down for a chain up to a terminal at 26566 from which side lines can easily be written down. The two long e links are naturally represented by  $e(-\delta_1)$  with simultaneous displacements in other links. At 41500 (f. 3) there is a typical

parallel inequality correcting both the links attached to it. In this chain it is to be noted that the several u, v links are all normal with the exception of that between Nos. 2 and 7, which requires a displacement  $2\delta_1$  on a d link. The X. iii. map contains a large number of symmetries showing meshes involving the 1000 and 14333 separations, or the diffuse links indicated by arrows and broken lines—see, e.g., the neighbourhood of (e. 1) and (f. 6). A very striking illustration of such symmetry is afforded by the system attached to 27758 (c. 7). It is represented in the following scheme:—

			31804	
			1493	6.44
28755	* * *	17263.02		46020
1494	1.33		1002:30	
	43697			
997.14				1002.53
			30082	
	1002:22		1493	86.21
27758		17259.63		45018
1493	6.25			
	42694			

The agreement in the values of each separation is very close and would be wholly so if 28755 were about 5 larger. As the X. iii. map contains the  $D_{12}$  linkage the term VD occurs in the formula for 27758 and the 1002 is due to a  $\Delta$  displacement in this. We have in fact two parallel linkages depending on  $D_{12}(2)$  and  $D_{12}(-\Delta)$  respectively. A similar case is seen in the neighbourhood of X. iv. k. The close equality of the differences between 26842 and the next lines, viz., 46'46 and 46'49, is noticeable and has been already referred to. Now 46'46 is caused by a displacement  $+4\delta$  on  $VD_{11}$  and  $+4\delta$  on the same. As the VD enters in the formula as a negative quantity, the smaller wave-number would be due to  $+4\delta$ 0 and the larger to  $+4\delta$ 1.

The maps bring out certain general peculiarities quite clearly. Amongst these may be mentioned:—

- (1) The majority of the strong lines are connected to the e link either directly or by an intermediary p link. More especially so in the case of Ag.
- (2) The curious frequency with which, in a mesh involving the e link, a u or v link is attached at one angle. In many cases we find u or v links attached to an e link as if the whole of a mesh has not been observed.
- (3) The fact that where a large number of links converge on a line, that line is in general of small intensity—suggesting that the number of configurations present emitting the frequency is small, because it is only slightly stable and splits up into others related to it by the link relation.
- (4) The large number of p links of normal value entering in the D linkages.

The evidence given in the preceding pages would seem to establish conclusively the existence of these links and linkages in the spark spectra at least of Ag and Au. Of 740 lines in Au only 41 have no p, s, 1000, or 14333 links attached to them, whilst 100 others with links have not been allocated to the linkages exhibited in the maps. It is noticeable also that of these 100, the majority show the 1000 and 14333 links, indicating that they have relations to diffuse sequences—not here discussed. Of 600 lines in Ag only 92 show none of the p or s links, of which 54 occur in the first 60 and last 30, where the fainter lines which might complete links are not observed through photographic and instrumental difficulties. In addition, about 110 are not allocated to definite linkages in the maps. We should expect many of these—from analogy with Au—to have reference mainly to linkages related to diffuse sequences.

The complete problem of the relations involved and criteria for true and spurious links, is one involving a much more exhaustive treatment than that given in the present communication. It will necessitate the consideration of the D sequence links, and especially of lateral displacements, the existence of which the present discussion has clearly indicated. The cause of the variations in the magnitude of the links themselves must be discovered and will require a more accurate determination of wavelengths and of possible observation errors. These questions are reserved.

FORMULÆ TABLES.

AgS (2).

				ASO (4).	• (,						
		$v$ ( $\Delta$ ).	p.	$p(-\Delta)$ .	$p(-\Delta)$ . $p(-2\Delta)$ .	$p (-3\Delta)$ .	$s(\Delta)$ .	8.	$s(-\Delta)$ .	\$	dλ.
1 2 (6)	12082 920·79 13003		—	F						<u> </u>	
	$4781 \cdot 37$ $17784 \cdot (\cdot 52)$ $959 \cdot 49$	-(-1)		П	Γ	1 + (-1)					- 17
4 KO	-966.09 -966.09 17778 (19)	-1 .		_	-(1)	2 (1)					90. –
6 (2)	5074·08 18077 (-1·17)			7			-1		7		36
				AgS (3).							
г	$S_2(3) = 22833.79$			_							
2 (9)	$S_1(3) = 920.42$ $S_1(3) = 21413.37$		П		-						
3 (7)	20450 (·1) 010:84			_	-						.02
4	21370 (·70)			ଚା							.15
2	18756 (·30)			ଟୀ	-1			(1)	-(1)		
9	17874 (-36)	П		c1	Ę.			_			10
7 (3)	$22911 (\cdot 49)$ $17638 \cdot 98 (\cdot 80)$	(-1)		П	- 1	- (-1)	-(-1)	(-1)		<u> </u>	.32
9 (2)	21413 21413 2770.00		_	#							
10	25192 (-32)	-(-3)	_			(-3)					<u> </u>
11 (27)	$28968 (\cdot 20)$ <b>2461</b> · 12	-(-3)-(-2)				(-3)+(-2)	~			-	.03
										_	

AgS (3) (continued).

δ'. (λλ.	-1 .00	-1 .09	-105	-1 - 15	-1 .03	-109	-102	- 1 .02	-106	-1 .02	-1 -11	-117	-115	-1 -01	-1 .00	-1 .05	-103	_1 - 05	. 1 .00	-101
$s(-\Delta)$ .	1			<u> </u>	 	·	- 1		1	(-1)	(-1)	1	1					*	1	
8.	_	1	$\vdash$	H	-	ទា	ಣ	ଟୀ	ণ	2 - (-1)	2 - (-1)			П	П				П	
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$p(-2\Delta)$ .		П	П	1	ଟୀ	1	П	1	1	1	ଚୀ	1	1	(1)	1 + (2)			-(-3)	-(-2)	-(-1)
$P(-\Delta)$	1	1	61	ec -	<del></del>	- 3	- 3	6-	- 3	<del>හ</del>	4 -	- 61	<u>.</u>		- 1	-	ପ	61	67	ଟୀ
p.	1	Т	टा	ಣ	೧೦	ಣ	ಣ	ಚ	69	ಣ	ಣ	ଫ	ଟ୍ୟ	1	1		- 1	- 1	- 1	1
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	31429 (03)	32390 (·99)	-919.00 $31471(-45)$	$-919^{\circ}90$ $30552(-1\cdot39)$	31513 (+·31)	$33010 \; (-\cdot 97)$	-2017.81 $30393 (23)$	29236 (·17)	36789°64 36789°46 ( - ·84)	39409 (·37)	40370 (1.78)	-2457.67 $29014 (-1.42)$	25237 (93)	$-1000^{\circ}45$ $30422 (-\cdot13)$	31385 (·07)	29888 (·45)	30806 (-35)	$31815\ (-\cdot 54)$	$2425 \cdot 51$ 34271 (0) $9464 \cdot 70$	-
	12 (25)	13	14 (23)	15	16	17 (15, 19)	18	19 (15)	20 (15)	21	22	23 (14)	24	25 (12)	36	27 (11)	28 (32)	29	30	31

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AgS	

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28	27798 (·56)			П	-1-(1)		-		F-4	20.
99	982:23 287:60 (.98)				-(1)		1	П	-	.10
30 (27)	$-900.36$ $29454(-\cdot14)$			2(1)	-3(1)		<del></del> 4	- 2	7	01
31	32073 (- · 13)			2(1)	-3(1)			-2-(-1)	2 + (-1)	01
32	31064 (·08)			2(1)	-2(1)	-(1)	1	ا ش	ಣ	.01
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	p.					<i>p.</i>			<b>-</b>						Γ	П	1	<u> </u>	
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40 33316		1	63		-			-2(-1)	2(-1)	$-d_1$	.01
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	ď.	$-d_1$	- 111	$-d_1$	$-d_1$		ď.	- d <sub>2</sub>	$-d_2$	$-d_2^*$	$d_2$	$-d_2$	$-d_2$	$-d_2$	$-d_1$	$-d_2$	$-d_2$	$-d_2$	- d <sub>2</sub>
	$s(-\Delta)$ .	(-1)	2(-1)	2(-1)	(-1)		$s(-\Delta).$								(-1)		_	_	_
	8.	-(-1)	-2(-1)	-3(-1)	-(-1)		. *\$				-(1)	- 1			-(-1)			2	c1
	$s(\Delta)$ .			(-1)			$s(\Delta)$ .				(1)	1							1
	$p(-3\Delta)$ .	_	1	Ţ			$p(-3\Delta)$ .			_	_				-	1	-		<i>→</i>
(x) (x) (2)	$p(-2\Delta).$			)—( 		AgD (5).	$p$ $(-2\Delta)$ .			-	1		_	_		-	1	1	Ţ-
- Cart	$P(-\Delta)$ .	(2)	-(2)	-(2)	- -		p(-1).			<i>-</i>	r-t		T		- 1	7	_	posed	СТ
	<i>p</i> .	2+(2)	2 + (2)	2 + (2)		<b>t</b>		, , , , , , , , , , , , , , , , , , ,							_	_	<u>~</u>	<del></del>	
	$p(\Delta)$ .		- 1	1 -	1		$p(\Delta)$ .										7	-	-
		29822 (+23)	$2619 \cdot 44$ $32442 \ (-15)$		922·10 29863 (·47)			(6) $D_{12}$ (27585 · 33)	$920 \cdot 44$ $(28505 \cdot 77)$	1008 · 8 29514 (	. ~	959·54 28016 (·23)	962·60 28547 (-·06)	80.086 80.086	2620·15 31168		<b>2617·81</b> 33010 ( - ·41)		919·50 31471 (·44)
		44	51	52	53 (43)			1 (6) D <sub>12</sub>	$2$ $D_{21}$	3 (9)	*	ıΩ	6 (1, 8)	1	8 (6)	9 (3)	10	11	12

\* Or if  $-d_1$ , the error would be very small.

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d\lambda.		e.	$\cdot 15$	.01	25	30	.01	90. –	80.	00.	.05	. 20	12	.19	.14	.03	61
, o,		-	1	-	_	7	-1			Ţ	-	-	- 1	1 1	-	-	
$s(-\Delta)$ .							1										
s.								-2-2-	a approximate				_	enaker e			_
$s(\Delta)$ .						1											
$p(-3\Delta)$ .					7	7	-	_		,—·	ÇI	c1	The second sections of the second section section sections of the second section section section sections of the second section section section sections of the section	$\begin{pmatrix} -1 \\ -1 \end{pmatrix}$	(-1)	(-1)	(-1)
$p(-2\Delta).$			1	7	¢1	ςī	¢1	-	<u>-</u>				(-1)	(I)			
$p(-\Delta)$ .	_							П					-(-1)	-1 $-(1)$			7
<i>p</i> .	1	- (-2)	(-3)	-2(1)	-2 (1)	-2 (2)	-2 (1)	-(-2)	- 1	<u>.</u>	- 1		-		_	ĭ	<del></del>
$p\left( \Delta\right) .$		(-2)	(-2)	2 (1)	2 (1)	2 (2)	2 (1)	(-2)		_				$-\begin{pmatrix} -1 \\ -1 \end{pmatrix}$	-(-1)	-(-1)	-(-1)
	20776 3815 24592	-3199.63 $21392 (1.1)$	26000 (1)	-3187.41 22813 (·07) 5624.52	17178 (- · 76)	28525 (-2·46)	13457 (·30)	27029 (- · 37)	43257 (1·53) -3403.63	40063 (*02) 5625.72	48892 (1·13)	52088 4641.39	25387 (-·81)	17530 37 42644 (3·51) or (·76) 4606.95		26698 (·25) —14039-95	$27711 \ (-1.48)$ .
	1 (14) $S_1$ (3) 2 $S_2$ (3)	3 (9)	4 (10)	ıq	9	1	$\infty$	9 (3)	10 (4, 12)	11	12 (10)	13	14 (1)	15 (18)	. 91	17	(12) 81

	dr.	11	.01	36	20	16	20	₹6.	01	00	.10	.05	90.	60.	.03	.20	<u> </u>	01	.01	.00
and the second s	, xc	- 1		- 1	:	-	1	-		-	-		-	-		-	1		-1	1 - 1
	$s(-\Delta)$ .		Ī	L C1	2 -	2 -	- 2								,—(	, , , , , , , , , , , , , , , , , , ,				
	જ	_	-	63	67	2	¢1								-	~				
The second secon	$s(\Delta)$ .																			
	$p(-3\Delta)$ .	(-1)	• $1 + (-1)$	2(-1)	1 + 2 (-1)	1+2(-1)	1 + 2 (-1)			(-1)	(-1)	(-1)	(-1)			(-1)		ςī	C1	ಣ ಣ
AuS (3) (continued).	$p(-2\Delta)$ .	CJ				-(2)	- (2)	-(2)	(3)	-						-(2)	7	-	-	
AuS (3)	$p(-\Delta)$ .	ç1 	-	-(-1)	- 1	-1+(2)	-1+(2)	1 + (2)	2 + (2)	ಣ	©I	_	,—(	r—	<del></del>	2 + (2)		1	1 - (-1)	
	<i>p</i> .	~	-	·	_	-			-	<u> </u>	-1		(1)	(8)	(4)	1		1	1 + (-1)	2 (1)
	$p\left( \Delta\right) .$	-(-1)	-(-1)	-(-1)	-2(-1)	-2(-1)	1-2(-1)			-(-1)	-(-1)	-(-1)	-(-1)-(1)	-(3)	(4)	-(-1)	। ७३	61	ଟୀ	$-2 (1) \\ -2$
		82378 (-1.09)	33345 (·09)						23805 (- ·09)	17258:49 41064 ( ·05)	4603 : 20 45669 (2·09)	41855 (-9)	3188	27783 (-68)	_				- 3817 70 46859 (·33) 5693-60	52492 (·08) or
		19	20 (18)	21	55	ମ ଦୀ	<u> </u>	25	26	27 (33)	28	29	30 (34, 35, 43)	31	829	33 (27)	34 (30)	35 (30)	36 (38)	37

	$d\lambda$ .	90. –	13	.10	10	01	03	.03	90.	28	77.	01	.01	.03	03	80. –	80. –	15	10	.03
Andrew of the control	,°S	<u>.</u>	1		Ţ	-	-	1	<u> </u>		-	]					-	<u> </u>		
	$s(-\Delta)$ .	-	<del>,                                    </del>	7			-		- 1		-			- 2	7	-		H	_	-
Ť	s,*	7		1	_				<u>-</u>					63						
1	s (\(\Delta\).																	-	- 1	
-	$p$ ( $-3\Delta$ ).	67	Ç1	<b>C3</b>	2-(-1)	67	(-1)	1 + (-1)	c1	П	1 - (1)	1 - (1)	2 - (1)	1 - (1)	(-1)	7	4		-(-1)	- ( - 1)
AuS (3) (continued).	$p$ ( $-2\Delta$ ).	- 1	- 1	-1-(-1)		-	•				(1)	(1)	(1)	(1)		- 23		7		1+(-1)
AuS (3) (	$p(-\Delta)$ .	1-(-1)	1-2 (-1)	1 - (-1)	1 - (-1)		П	_	П	П	П	_			टा	73				-1 - (-1)
- The second sec	<i>p</i> .	1+(-1)	1 + 2 (-1)	1+2(-1)	1 + 2 (-1)	73	(3)	(3)				( - 3)	(-2)	(-4)	(3)	(-1)	1	H		
	$P'(\Delta)$ .	GT	- 2	63	c)		- (-1)-(3)	-1-2 (1)	i cı			-1-(-3)	-2-(-2)	(4-)-6-	-2(-1)	- [ - ( - 1)			(-1)	(-1)
		. •	. ~ .	23495 (·56)	7857 (- ·31)	<u> </u>									~ .		36727 (-1.07)		34400 (-1·21) 4600.09	39009 (·29) 5631 · 98
		38 (36)	39 (42)	40	41	42 (39)	43 (30, 51)	44	45	46	47	48	49	50	51 (43)	52	53 (66)	54	55 (68)	56

AuS (3) (continued).

dλ.	ço.	60. –	.10	.05	.05	96	• 00	03	00.	<u> </u>	.01	00.	61.	.01	90. –	<u>ç</u> 0.	.01	.03	00.
, *8	<u> </u>	-		- 1		-		-	- 1	-1	-	- 1	- 1	- 1			- 1	- 1	
s ( - \D).	_	_		_	<del>,</del>	<u></u>	63	ଦ୍ୟ		-	ÇI	p==4	7	-	7	_	г	_	-
\$							-	-			-								
$s(\Delta)$ .	- 1	[	-		-	- 1	-	- 1	- 1	-	1	- 1			- 1	- 1	-		ī
$p(-3\Delta)$ .	c <sub>3</sub>	cī l	63	-(1)	- 1	-1-(-1)	-1-(-1)	-1-(-1)		-(-2)	-(-2)	-(-1)	-(-1)	(-1)	- 2	2		2	- 2 (- 1)
$p(-2\Delta).$	ಣ	ಣ	ಣ	က	?ì	2	63	¢1	¢ì	1 + (-2)	1 + (-2)	1 - (1)			4	ŭ	ro -	4	4 (-1)
$p(-\Delta)$ .	-1-(-1)	- (-1)	1 - (-1)	1 - ( - 1)	-(-1)	- 1	- 1		- (1)	-1		-1+(1)			-2-(-1)	-3-(-1)	-2-2(-1)	-1-3(-1)	-5 (-1)
<i>p.</i>	p=4		- 1					(3)		П	П	_	_	1 - (-1)	_	-	(-1)	(-2)	2 (-1)
$p(\Delta)$ .	(-1)	$\begin{pmatrix} -1 \end{pmatrix}$	(-1)		(-1)	1 + (-1)	1 + (-1)	(-1)				(-1)	(-1)	2(-1)	(-1)	(-1)	1 + (-1)	1 + (-1)	1 + (-1)
	(F	37195(-1.26)	41007 (1·62)	1720% 58271 (1·65) 5823.05	42828 (1·0)	-1651 for $-1.75$ )	40505 (·81)	48697 (- · 59)	60074 (0)	31084 (- · 46)	46020 (·31)	-4600.20 $29794(-03)$	$-11045 \cdot 36$ $18449 (\cdot 41)$ 2100 : £4	26595 (·08)	37987 (-·84)	42593 (·99)	25337 (·10)	30970 (·17)	
	57 (71)	58 (61)	59	09	61 (58, 65)	. 65	63	64	65 (61)	66 (53)	1-9	68 (55, 68)	69	70 (68)	71 (57, 76)	72 (79)		74	75

continued
3)
AuS (

		$p(\Delta)$ .	<i>p</i> .	$p$ ( – $\Delta$ ).		$p(-2\Delta).$ $p(-3\Delta).$	$s$ $(\triangle)$ .	s,	$s(-\Delta)$ .	, °,	dλ.
76 (71)	5637·56 43624 (·80)	-		೪	ಖ				П	7	•0•
22	28689 (-1.38) -11339.90	_	П	ا دی	ಣ	- 1	1	-		-	16
78	17349 (- ·11) -14931-43	Г	П	ا ئ	2 + (1)	-(1)				- 1	03
79 (72)	27661 (- · 43)	П	-	- 4	2	c1	- 1	7	61		90. –

AuP(1).

										Plant of Assert Asse
dly.		2.	. 58	.05		00.	.03	.01		90. –
$s(-\Delta)$ .							<b>→</b>	<del></del>		
ం .	-	-				<b>-</b>			_	
s (△).										
$p (-2\Delta).$ $p (-3\Delta).$				7	2(-1)			(-1)		( - 1)
$p$ ( $-2\Delta$ ).		0		i		-	-(-1)	-2(-1)		
$p(-\Delta)$ .	-		-	1	_			-		
p.						-(2)			1	
<i>p</i> (Δ).		-	Г		-(-2)	(-2)	(-1)	<i>-</i>		-(-1)
	37357 —17256·66	$\begin{array}{c} 20100 \ (2.88) \\ 5636.31 \end{array}$	$25736 (1 \cdot 90)$ $17254 \cdot 67$	42991 (1.02) $17279$	$60270\ (-4)$ 3813 $\cdot$ 98	29550 (.06) 14932.07	$40668 (\cdot 45)$ 5130 · 16	$46299 (\cdot 20)$ 3815.74	41172	58438 (-2) -14941
	$P_2(1)$								$P_1(1)$	
	1 (16)	C1	3 (6, 7)	4	J.C	6 (3)	7 (3)	8	9 (1)	10

AuP (1) (continued).

		$p(\Delta)$ .	p.	$p(-\Delta)$ .	$p(-2\Delta).$	$p(-3\Delta).$	$s(-\Delta)$ .	\$	$s(-\Delta)$ .	$d\lambda$ .
11 (15, 17)	$43497 (2) -17260 \cdot 74$	- (1)	- 1			(-1)		c1	1	.10
12	26236 (-1·29)		- 1					¢ί	- 1	18
113	21629 (.67) $3106.69$			(1)	-(1)			67		.14
14	1848.2 (- · 09)	<u>-</u>	cı	-				¢য	- 1	03
15 (11)	00755 (0)	-1 - (-1)		,		1 + (-1)		¢1	-	00.
16 (1)	54617 (*54)	<u>~</u>		-(1)		(-1)		_		.01
17 (11)	40305 (- · 8)	1 - 1(-1)	c3			(-1)	-	23	- 1	90. –
18 (20)	34669 (-13)	1 - (-1)	C1		_	-1+(-1)		<b>©</b> 3	- 1	01
19		-(-1)	67			(-1)		¢β	- 1	13
20 (18)	$17410\ (-\cdot 24)$	-	-1-(-1)		(-1)			67	- 1	80. –
21	$\smile$ .	_	-1-(-1)		1	- (1)	-1	ಬ	-	<b>70.</b> –
<u></u>	43687 (*91) 4605:43		6.1		(1)	-(1)	- 1	2		.05
23		_	- 5	(1)		-(1)	-	<b>c</b> 1		60.
24	42676 or	1 - (1)	-2+(1)	$\begin{pmatrix} 1 \\ 1 \end{pmatrix}$		-(1) - 1		ପ୍ର		. 58

i	dλ.		60.	03	.03	.03	00.	20.	80.	.10	01	21	00.	.03	20. –	4 .15	80.	90.	<b>*</b> 0. −	<del>+</del> 0. –
	$d_2$ .	<del></del>		_	=		1	1	1	1	1		П		=	_	_	Π	1	1
-	\$ ( − △).																			
AuX.	&												1	1			П			
	<b>s</b> (\(\Delta\).														-		1			
	$p \ (-3\Delta).$		П	ଚୀ	2 + (1)	3 + (1)	δ	4	3 + (1)	2 + (1)	4	proof	1	П	_	_	П	_	1 + (1)	1 + (1)
	$p \ (-2\Delta).$			-(-1)-1	· ්	*-	-4-(-1)	-4-(-1)	-3-(-1)	-3-(-1)	-2-2(-1)		_						•	
	$p(-\Delta)$ .		7	- (1)	(1)	-(1)	-(1)	-(1)	-(2)			Ç1	c1 	- 2					-(1)	-(1)
	<i>p</i> .				1			1-(-1)		-(2)	-(2)			(1-1)	-1-(-1)	-		-1-(-2)	- 2	00
	$p$ ( $\Delta$ ).							(-1)	П	_				(-1)	(-1)		- 1	(-2)		_
		15923	21558 (·41)	27191 (- · 24)	32882 (-34)	38457 (·38) 5620.46	44097 (-12)	$\sim$	21201 (·37)	25012 (·67)	42270 (- · 28)	26167 (-1·44)	37508 (·09)	$34311 (\cdot 23)$	38127 (-31)	$41325 \pm x$	44517 (1·64)	26782 (-47)	44033 (- ·79) - 3105-16	
	-	1 (25)	2 (11, 36)	ಣ	<del>~ </del> 1	2	9	7	$\infty$	6	10	11 (2)	13	13	14 (17)	15	91	17 (14)	18	19

AuX (continued).

	dλ.	80. –		90	80	02		<u>ç</u> 0.	.13	90.	11	.02	30.	20	.05	.03	80	00.	00.	00.
	$d_2$ .	1	$d_1$	$d_1$	$d_1$	$d_1$	1		<u>-</u>	_	-	<del></del>	1	Ħ	1	7	<u> </u>		П	7
1	s ( \( \Delta \).	-			F	- 1			1	H	7	7	cı	જા	ទា	¢ι	ទា			
	S°	7			<del></del>	-		٠	-	- 1			-	- 1	- 1	- 1	- 1			
	s (\(\Delta\).											1		-	1	<b>⊢</b>	-1			
	$p(-3\Delta)$ .	1+(1)		_	_	_		7	1	1 - (-1)	1 - 2 (-1)	-(-1)	(-2)	-2(-1)	-2(-1)	-1-2(-1)	_ 3 - (-1)	¢Ί	Ġĩ	ÇI
	$p(-2\Delta)$ .					(-1)								_	-	(-1)	ତୀ	-(1)	- 1	-1-(1)
1	$P(-\Delta)$ .	-(1)				-(-1)				-1+(-1)	-1+(-2)	-1+(-1)	-1+(-2)	-1+(-2)	(-2)	(-1)	(-1)	-1	(1)	
	<i>p</i> .	-2-(1)	-1	-1	-(2)	-(2)	- 1	- 1	- 1	- 1		-(-1)	-(-1)	-(-1)	-1-(-1)	-1-(-1)	-1-(-1)		1	(1)
	$p(\Delta)$ .	(1)			(-5)	- (-2)		- 1	-		7	(-1)	(-1)	(-1)	(-1)	1 + (-1)	-1+(-1)	-(-1)	-1-(-1)	67
		35903 (-+54)	19118	36367 (-82)	-14934.20 $21433(-38)$	26048~(-11)	19738	36991 (-67)	14934.25 51926 (3.66)	34669 (75)	17410 (-35)	28755 (-22)	14931 22 43687 (+38)	$-2053 \cdot 93$ $38053 \cdot (-1 \cdot 0)$	41866 (-85)	24616 (·15)	-5051.25 18985 (- · 30)	38818 (- · 11)	42016 (*12)	37410 (0)
		20	$21 (1)   D_{11}$	22	. 53	£24	25 (1)	36	16	80	66	30	31	32	33	34	35	36 (2)	37	38

2
AuD11

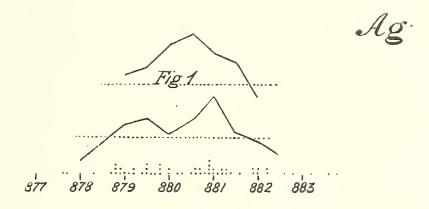
$d\lambda$ .		20. –	00.	.04	90. –	10	.01	00.	03	60.	90.	.05	90. –	01	01	.01	02	.01	00.	90.	01
$d'_1$ .	-		-	7			7	7	7	-	T ====	1		-		į			7		-
$s(-\Delta)$ .																	1	П	কা		$\vdash$
Š											- 1	- 1	- 1			- 1		- 1	67	-	
s (\(\Delta\).						-					-								•	,	
$p$ ( $-3\Delta$ ).					-	<u> </u>												- 2	6		
$p$ ( $-2\Delta$ ).					1	-	(-1)	1 + (-1)	ଚୀ	ପ	1 + (-1)	1 + (-1)	(2)		1		67	က	ಣ	· · · · · · · · · · · · · · · · · · ·	
$p$ $(-\Delta)$ .			П	T	1	1	1						(1)	- 1	- 1	- 1	-(-1)	-(-2)	-(-2)		
77.		1 + (2)	(1)	1 + (1)	\$1	ಣ	ಣ	က	1 + (-1)	c1	2 + (1)	1 + (1)	1 + (1)	1 + (1)	1 + 2(2)	1 + 2(4)	(-1) + 2(4)	(-2) + 2(4)	(-2) + 2(6)	2(2)	1 + (1)
p (Δ).		-(2)	-(1)	-1-(1)	21	ا ش	-3-(-1)	- 3 - (-1)	-2-(1)	- 2	4	63	- 3	-(1)	-2(2)	-2(4)	-2(4)	-2(4)	- 2 (6)	-(4)	-(1)
		20317 (- · 28)	3816 · 92 24134 (· 04)	27329 (·32)	-5633.00 $21696(-31)$	3195.49 24891 (- ·66)		.01).			-11344.69 $35414$ (·81)	$-3194.83$ $32219 (\cdot 50)$	27615 (- · 47)	24926 (- · 09)	. ~ .	43047 (·21)	-3637.00 $37410 (29)$	31772 (*08)	46703 (005)	25250 35250	14938°78 35256
	$1$ $D_{11}$	2 (14, 20)	ಣ	₹	20	9	2	8 (11)	6	10	11 (8)	12	13	14 (2)	15	16	17	18	19	20 (2)	21 (2)

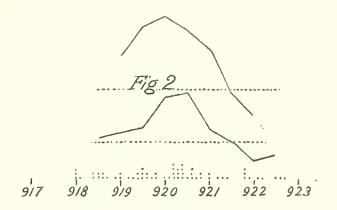
	dλ.		04	12	.01	00.	90. –	<u> </u>	00.	.05	.03	03	00.	04	03	÷0·	03
$\mathrm{AuD}_{\mathfrak{A}}(2).$	$d_2$ .	-	- 1	- 1	- 1	- 1	1	-	- 1	-	- 1	-1	- 1	- 1	-	-	
	$s(-\Delta)$ .							-	_	ទា	ଟୀ	c1	ତା	c1	61	<b>C</b> 1	
	တိ				П	П	_	-	<u>-</u>	ا دئ	ا دی	- co	ا د	ا ئ	67	67	
	$s(\Delta)$ .				- 1	-1	- 1		1	П		1	П	Ţ			
	$p$ ( $-3\Delta$ ).		1	1		1	1	(2)	(2)	(2)	(1) - (-1)	(2)	(3)	(1) - (-1)	(1) - (-1)	(2) - (-1)	(1) - (-1)
	$p(-2\Delta).$		- 1	-(1)	-(1)	-(1)		-(2)	-(2)	-(2)	-(1)	-2(1)	-2(1)	-1 - (1)	-1-(1)	-2(1)	$\begin{array}{c} -1-(1) \\ -2 \end{array}$
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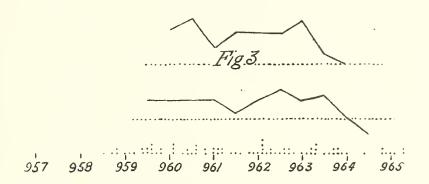
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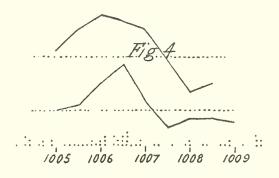
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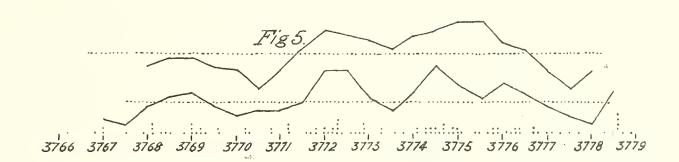


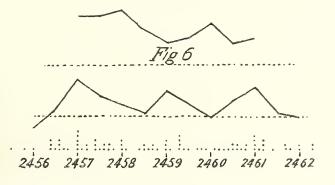


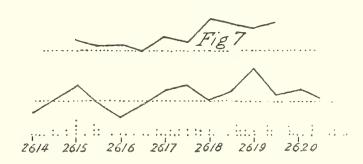






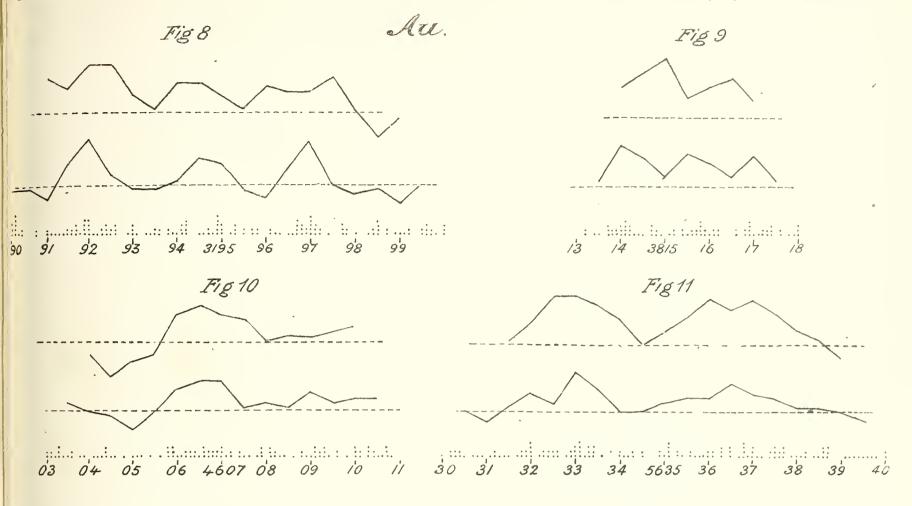


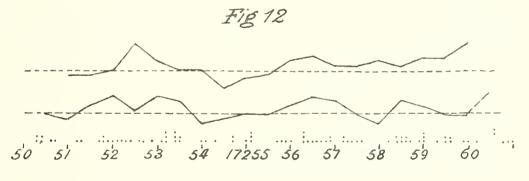


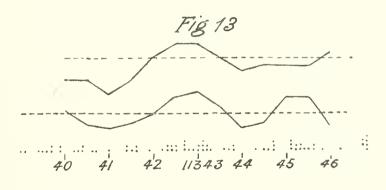


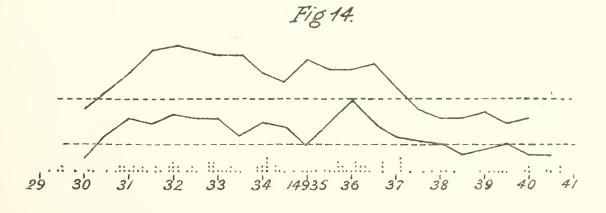


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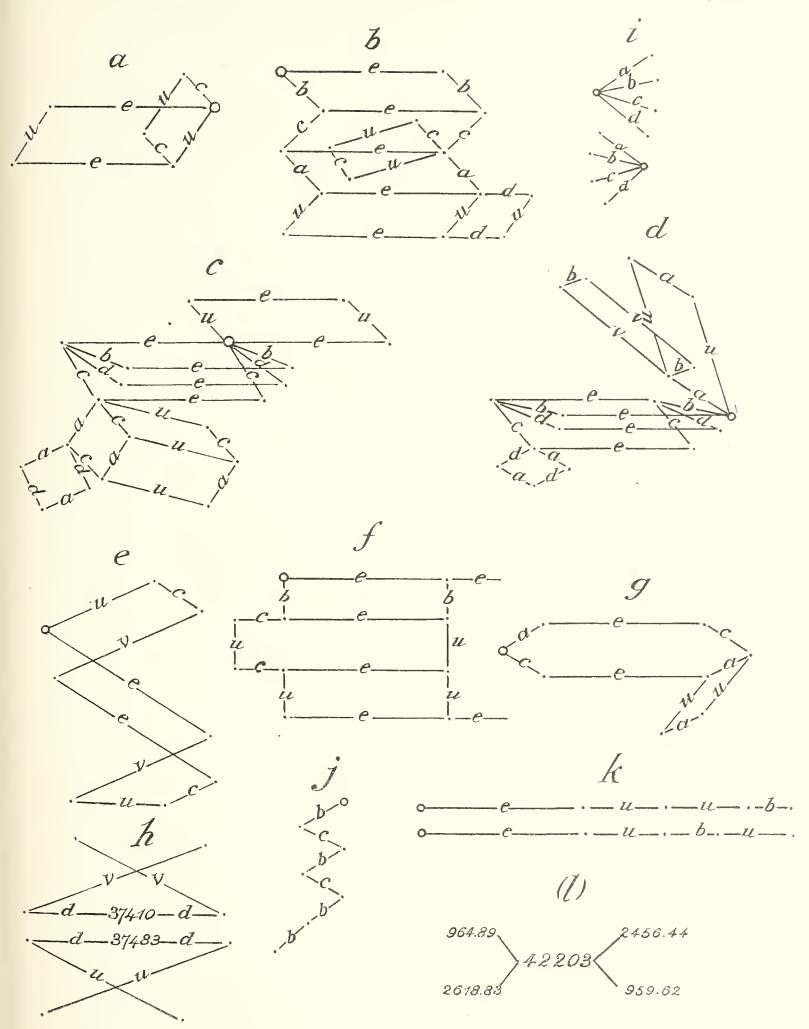


#### Notes to Plate 6.

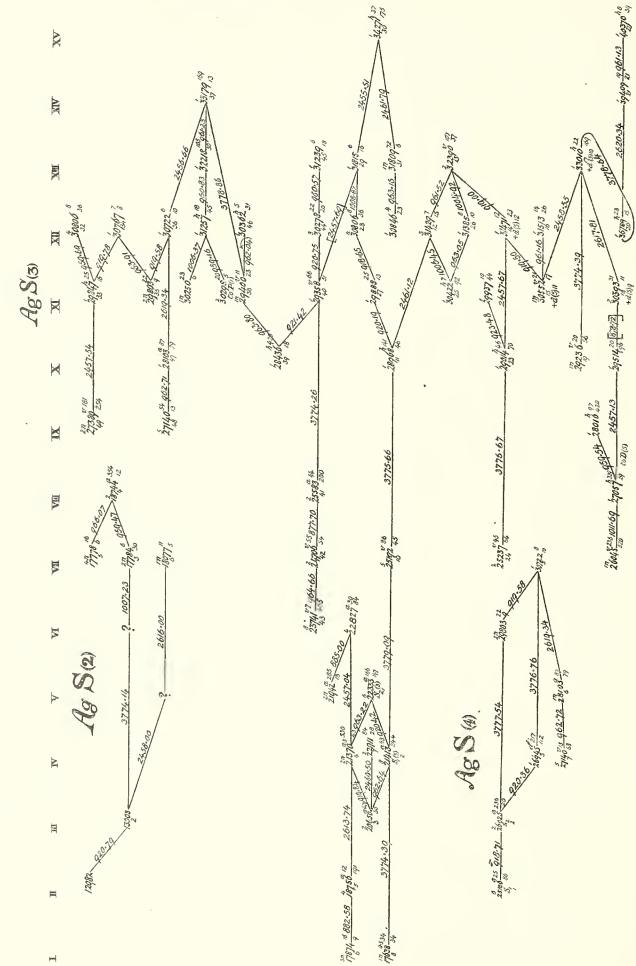
- (a) 43720 in the AgP linkage, two meshes on one link.
- (b) 25933 in AuX (ii.)
- (c) 38457 in AuX (iii.) showing complicated congeries of meshes; also see AuS (3).
- (d) 42068 in AuX (iv.)
- (e) 39150 in AgP (ii.)
- (f) 30029 in AgP (ii.) showing complete cycles of links.
- (g) 21696 in AuX (ii.)

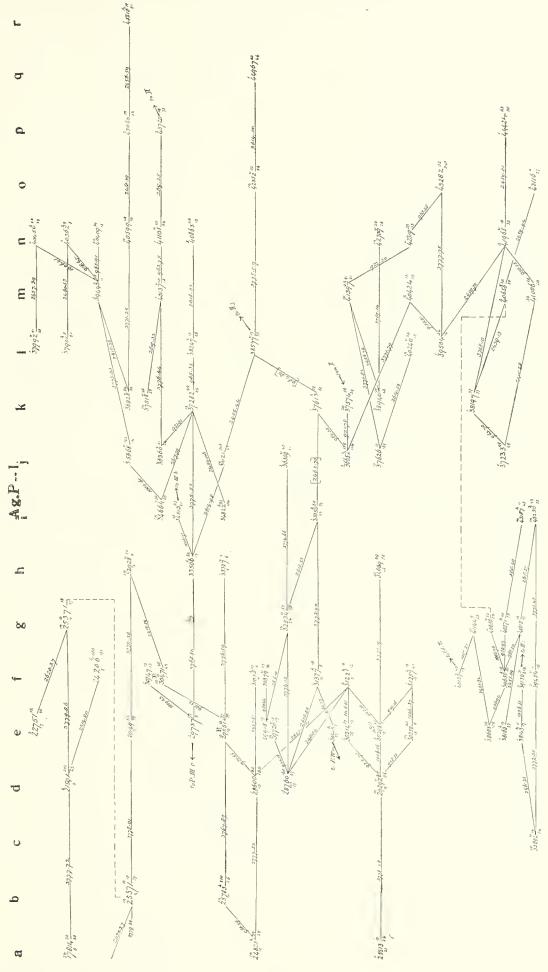
A similar one 19988 in AuS (3).

- (h) In AuX (ii.) shows parallelism and symmetry.
- (i) 21696 in AuX (ii.); 31967 in AuY, all p links diverging from or converging on.
- (j) 30722 in AgS (3) showing sequence -b+c-b+c-b-b.
- (k) 31494, 29216 in AgD (4) shows parallelism.
- (1) Correction to one line makes all four links normal.



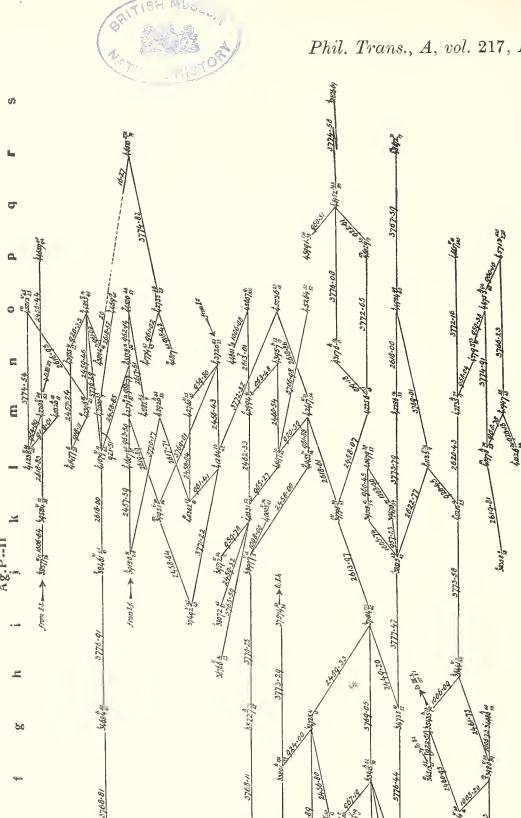


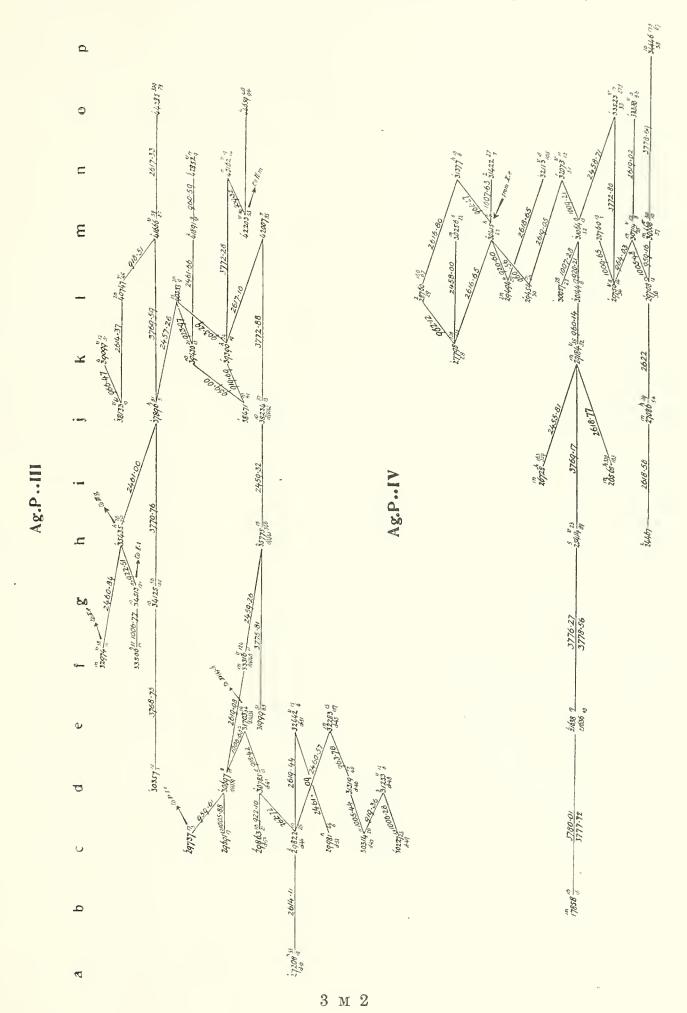


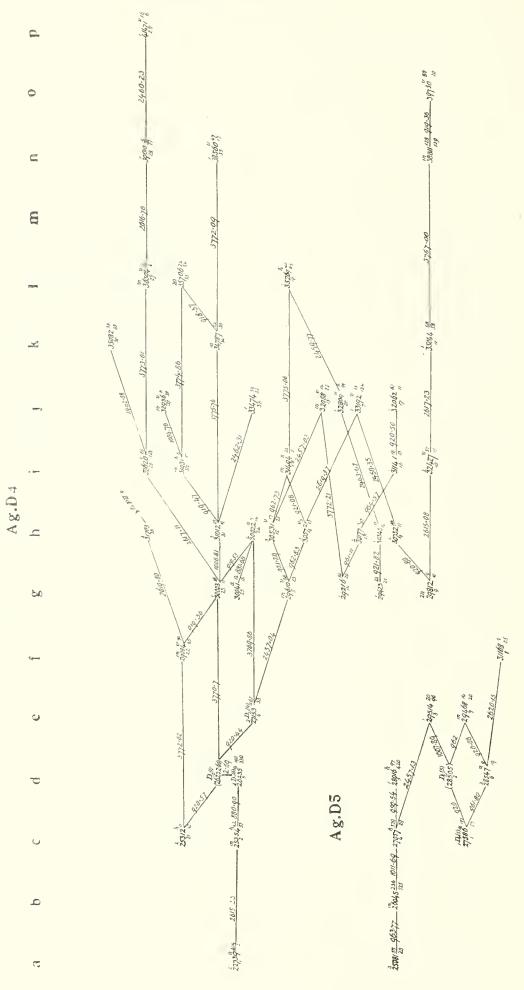


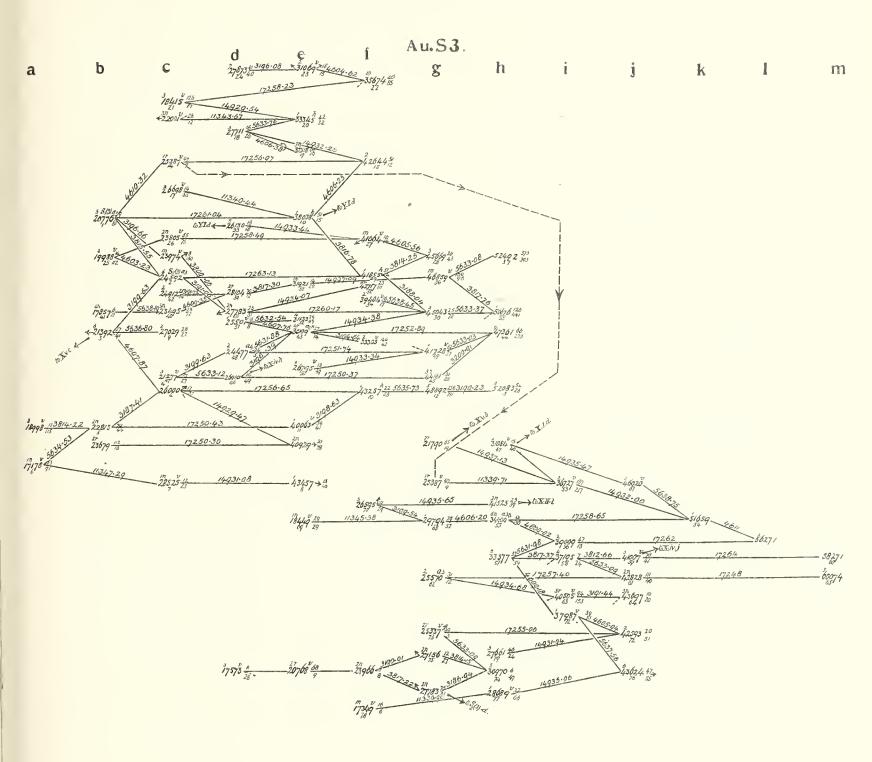
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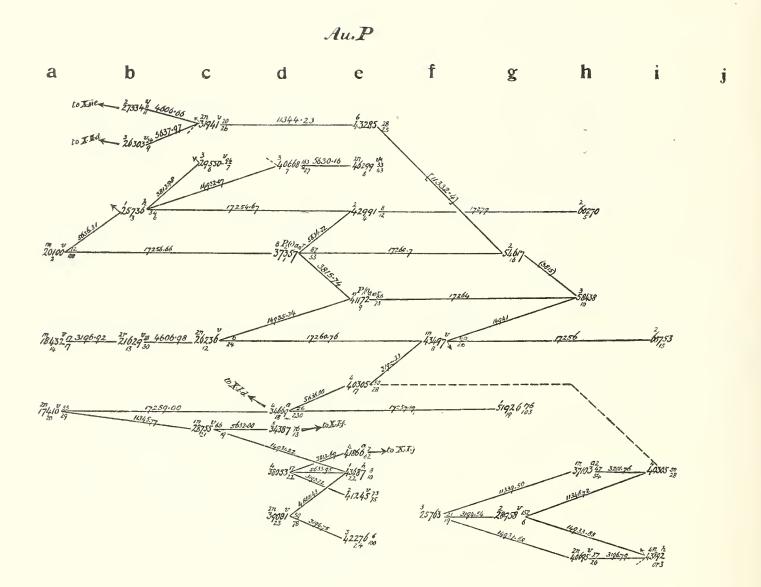


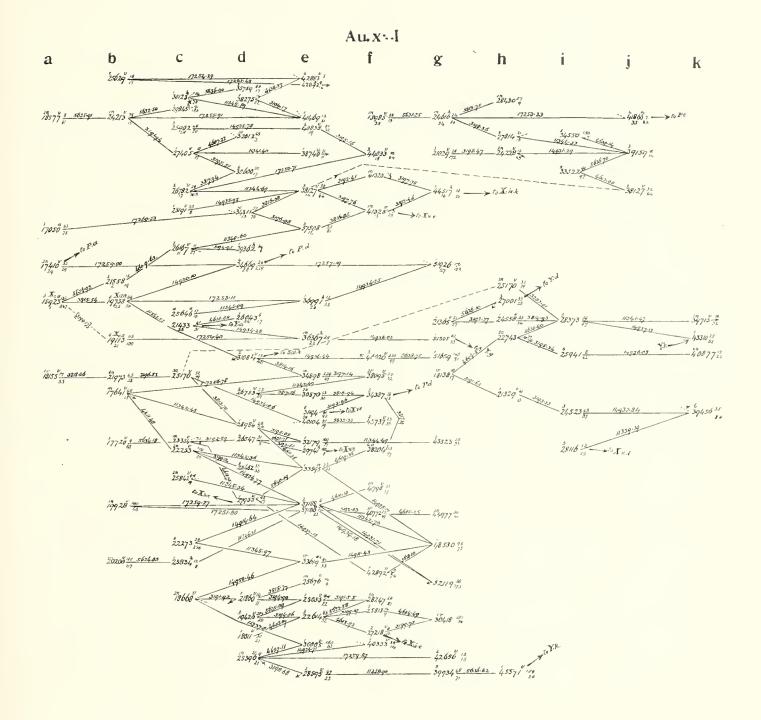




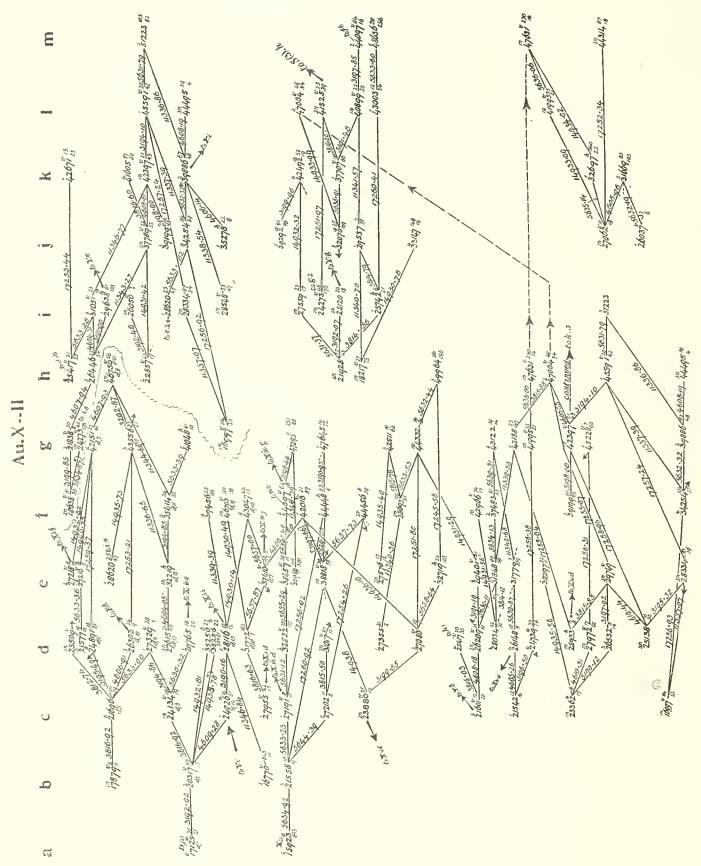


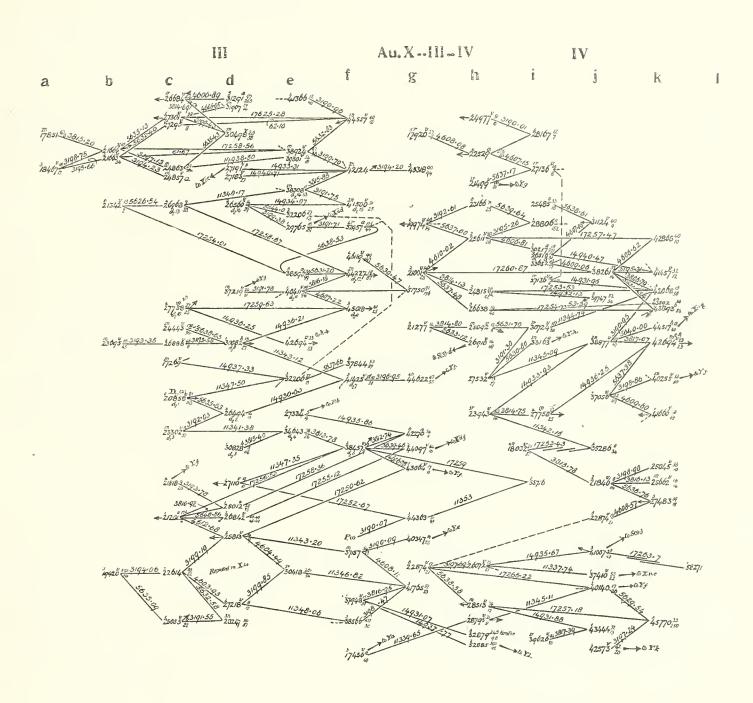






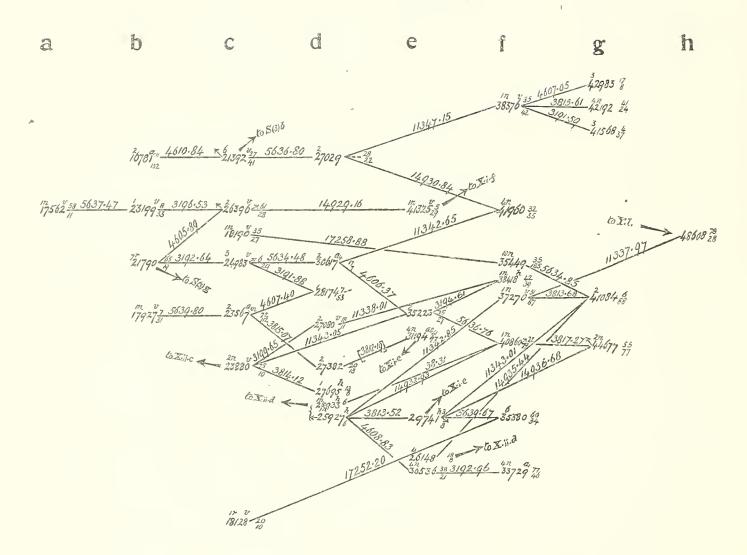


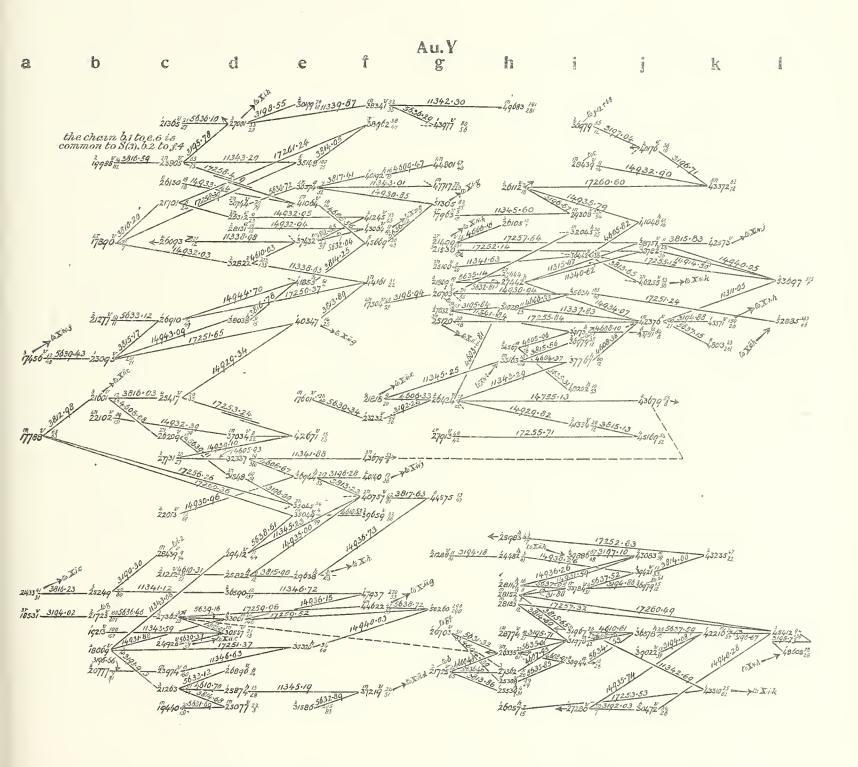






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SERIES A, Vol. 217. Pp. 411-430.

[PLATES 19, 20.]

# ON THE PHOTOGRAPHIC SPECTRA OF METEORITES.

BY

SIR WILLIAM CROOKES, O.M., F.R.S., LL.D., D.Sc., &c.

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# XI. On the Photographic Spectra of Meteorites.

By Sir William Crookes, O.M., F.R.S., LL.D., D.Sc., &c.

Received October 19,—Read November 2, 1916.

[Plates 19, 20.]

For several years I have been engaged on the spectrum analysis of Meteorites. Many meteoric specimens have come into my possession—through the kindness of friends—especially am I indebted to the Trustees of the Natural History Museum and to Dr. Prior, who presented me with specimens of such of the meteorites of which the quantity in their possession would not be appreciably diminished by the loss of the two or three grms. required for my experiments.

The Research is divided naturally into the examination of meteoric stones and meteoric irons. I propose at present to deal with meteoric stones or aerolites. These wonders of the sky consist generally of one or more silicates (mainly olivine and bronzite), interspersed with particles of nickeliferous iron, troilite, &c. Recent developments have led to many original devices and modification of details in the working spectrograph, thus furnishing information which may be of interest to those engaged on this branch of spectroscopic analysis.

As the whole value of the Research depends upon the excellence of my Spectrograph I propose to describe certain novel features of the Instrument. In previous papers I have already made brief reference to it, and therefore there is no need to describe it completely. It is peculiar in this respect; it has been devised and constructed in my laboratory for the work it was required to do, by a process of evolution, each part having been modified and improved as the work went on—thus in its present form it is the outcome of a great deal of experimental construction under working conditions. As an instance, I may say that the slit has been reconstructed at least six times—each change that the working conditions has rendered necessary making it more efficient until now it approaches perfection.

#### THE SPECTROGRAPH.

The instrument was originally devised for the photography of the ultra-violet region, but was ultimately extended so as to include the visible spectrum down to the limit of sensibility of the commercial panchromatic plate which is in the neighbourhood of

λ 7000 Å.U.; the two main aims in the whole construction were, first, that the definition of the lines should be pushed to the highest stage of perfection; secondly, that the mechanical construction should be such that the adjustments once made any number of spectra could be obtained without uncertainty in the excellence in definition. When I commenced to build the instrument, I was greatly assisted by the advice and suggestions of the late Victor Schumann. Although the instrument is very different in design to any constructed by him, still the experience he had gained in his researches upon the spectroscopy of the ultra-violet region, which he freely placed at my disposal, was of the greatest possible value.

Having decided upon the general plan, the instrument was built up, first temporarily in wood, afterwards permanently in iron and gun-metal—and set to work. This was in February, 1899, and since then it has been in continual use; some thousands of photographs having been made. During this period each detail of the instrument has been subject to a process of evolution and reconstruction, each step leading to some advantage demanded by actual work.

The parts of the instrument are all assembled upon a large truly surfaced cast-iron table measuring 31 × 51 inches; the dispersion is given by five excellent double prisms made of right and left handed quartz, each double prism consisting of two halves made respectively of left and right handed quartz, prisms such as were first used by CORNU to avoid double refraction.

The objective and collimating lenses are simple planoconvex, 40 mm. in diameter and 700 mm. focus. The spectrum is thrown upon a celluloid film so curved that all the lines are at their true focus.

The dispersion by the five prisms is considerable, and with the collimating and object lenses used would involve a spectrum of some 24 inches in length. As there are both mechanical and optical reasons against the use of such a large sized plate it was decided to "build up" the complete spectrum in eight successive plates, involving a length of 3 inches for each step. The reason for this decision is simple; to obtain perfect definition of any line it must be in or very near to the "optical centre" of the instrument, i.e., the imaginary line passing through the slit, the centre of the two lenses, the centres of the prisms, and the centre of the curvature of the plate: and it was found by many experimental photographs that the best definition over each three-inch film was obtained when the least refrangible line shown was in the position of minimum deviation. The many devices that from time to time have appeared in spectroscopic construction for rotating the prisms by link motion were rejected as uncertain and complicated—experiment having shown that the excellence of definition was maintained within a range of several inches on either side of the optical centre and position of minimum deviation. The exact "data" involving the focus, position of the spark, angle of the plate, and position of prisms and lenses to give the finest definition of the photographed lines were found experimentally, and when found their positions were engraved upon the instrument and recorded so that for future work

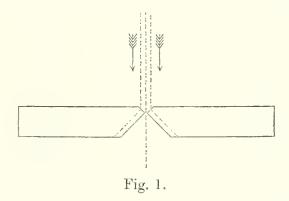
the instrument could be quickly set to give a photograph in perfect detail for any desired portion of the spectrum.

#### The Slit.

The slit—of necessity one of the most important parts of the instrument—has been subject to more alteration and modification than any other portion. On account of the close proximity of my chemical laboratory I decided at the outset to avoid the use of steel for this purpose; on this point I differed from Prof. Schumann, who was a strong advocate of hardened steel jaws, and all his splendid photographs were made with spectrographs having steel slits. I obtained good results by using rolled metallic cobalt—very hard and non-corrosive—ultimately I hit upon the plan of employing quartz instead of metal.\*

I find this substitute answers so perfectly that I cannot imagine anything better.

At first I had great difficulty in getting the edge true. The sides and angle must be ground true and polished. It is difficult to fashion a knife-edge of quartz at an angle of 45°, because small splinters occasionally break off. Ultimately I got over this difficulty by putting a very narrow bevel on the front of the plate, so making the angle of each jaw 90°, thus (fig. 1):—



Owing to refraction no light can get through the part of the quartz which is cut at an angle. The edge made in this way is absolutely black and opaque even in sunlight, and should bear a high microscopic power without showing irregularity. To prevent light from coming through the flat part of the quartz plate, the surface, all but the extreme edge, is coated with gold by cathode deposition. It is very beautiful to see the absolute opacity and trueness of edge of one of these slits when examined under a high power.

Jaws made in this way have now been in continuous use for many years and give perfect satisfaction; they are absolutely unaffected by the atmosphere, can easily be cleaned, and with common care do not wear out.

The width of slit I use is small; for general work I use 0.008 mm. only, but for years this very fine width was a source of annoyance and anxiety, the reason being

<sup>\* &#</sup>x27;Chemical News,' No. 1846, vol. lxxi., p. 175, April 11, 1895.

that it was necessary for purposes of adjustment, alignment of the spark, &c., to open the slit wide and then close it again. I found that even with the very best screws and construction there was always some uncertainty as to the absolute width of the slit used in any photograph—thus producing annoying variations in spectra, made at different times which should have been identical. During the first ten years of work many slits were constructed, each showing a slight improvement; even then the uncertainty was not completely removed and the mechanical construction had become deeply complicated. Ultimately the difficulties were removed by the device that I call the *Fixed* slit system. This device gives perfect satisfaction and has the advantage of extreme simplicity.

#### The Fixed Slit System.

Three such slits were prepared by taking brass blocks all of the same thickness, and upon each was permanently fixed a pair of quartz jaws set with openings of 0.008, 0.025, and 0.06 mm. respectively—these three widths being sufficient to embrace all the demands likely to occur.

The portion of the instrument upon which the slit is fixed is finished in the way shown in fig. 2; it carries two pointed pins, one of which appears marked C, a steel

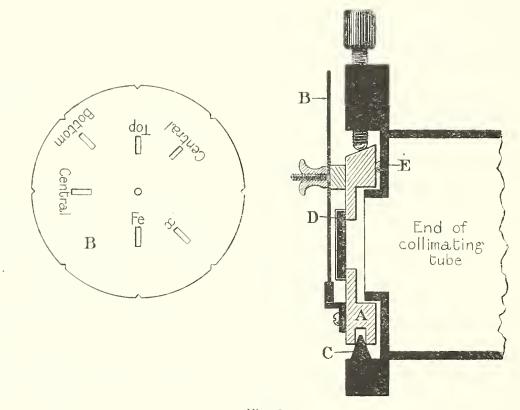


Fig. 2.

stop E, and a screw; the whole is closed to light except for a small rectangular central opening 1 mm. wide and 10 mm. long. A is one of the brass blocks carrying the quartz jaws D; this block can be instantly attached or removed by a slight turn

of the screw, and by the "hole, slot, and plane" device its position is invariable, as can be seen.

In front of the slit and attached to its plate is a circular brass disc B; this disc completely covers the quartz jaws D; it is pierced with several openings, any one of which can, by a touch of the finger, be brought in front of the slit and held there by a spring which engages in a notch—(as shown below).

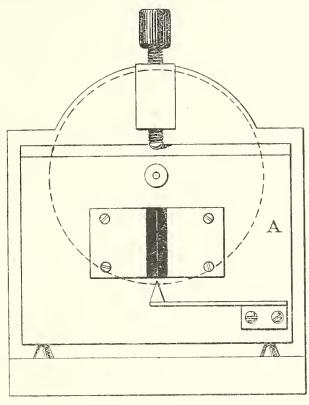


Fig. 3.

By these means light from various sources can be passed into the spectrograph through different portions of the slit and ultimately reaches the photographic film. For instance, in the particular work that forms the subject of this paper, the disc B is so fixed that the aperture marked Fe faces the slit, and the iron arc is projected upon it; then when a sufficient exposure has been given the disc is rotated so as to bring the aperture marked x opposite the slit, and the light from a silver-aerolite arc is passed in, the resulting photograph shows two spectra slightly overlapping, one of iron and the other of the silver-aerolite. No disturbance of the spectrograph or of the photographic film occurs during the operation.

A front view of the slit plate A is shown in plan in fig. 3; the dotted circle is the part covered by the disc.

The jaws do not wear or corrode. It is only necessary to clean and free them from dust by drawing between a sharply cut wedge of peg-wood.\*\*

Before enumerating the metallic constituents of the aerolites I wish to place on

<sup>\*</sup> Peg-wood splints are used by watchmakers to clean out pivot-holes in watches.

record the outcome of a research which, although not giving the expected result, furnishes information that may be valuable.

In connection with the several theories as to the origin of Meteorites it was thought that a thorough examination of the occluded gases might possibly reveal the presence of some of the inert gases, or of those hypothetical elements thought to be present in some of the hotter stars. At the present time the manipulation and spectroscopic investigations of gases have reached a high state of development, and a far more thorough investigation of the subject is possible than was the case years ago when much work was done by Prof. A. W. WRIGHT, of Yale College.\*

It is now possible and comparatively easy to separate from the gaseous mixture liberated by heating the meteorite, the hydrogen, oxygen, carbon compounds, &c., whose presence is not indigenous, and to reveal any of the non-valent elements that may be present. One of the most popular methods is to employ the process of absorption by charcoal at low temperatures—the same method that has been employed with so much success upon the gases contained in spring waters, &c. There are, however, certain experimental and manipulative difficulties that I wished to avoid.

Some years ago FREDERICK SODDY, Esq., F.R.S., published an account of a device in which the absorption by metallic calcium at its volatilisation temperature was made to answer the same purpose.†

Soddy's vacuum furnace, although a very ingenious piece of apparatus, is too elaborate for my purpose—so while adopting the principle I have modified the details.

The calcium cut into small fragments is placed in a small vessel of iron open at one end like a miniature test-tube and introduced into a similar but larger tube of fused quartz; it is then only necessary to attach the quartz tube to the pump and gas apparatus, and by applying a Meker burner so as to heat it to full redness the volatilisation of the calcium and subsequent absorption of the chemically valent gases are entirely under control.

By this means the gases—obtained by heating to redness each of the aerolites—were examined spectroscopically at different pressures. Fig. 4 gives an outline of the apparatus actually used. A special and simple form of Sprengel pump was made as shown, so that if needful it could be replaced by a new one for each meteorite. A is the vacuum tube; B the quartz tube with the iron vessel containing lumps of clean metallic calcium; C, a tube of hard glass, with the powdered aerolite; D, phosphoric acid to absorb moisture; E, an inverted tube filled with mercury in which any gas not used could be collected.

The procedure was to exhaust thoroughly, and well spark the vacuum tube so as to expel any gas occluded in the electrodes, and continue the exhaustion until the

<sup>\* &#</sup>x27;American Journal of Science and Arts,' 3rd series, 1876, p. 253.

<sup>† &#</sup>x27;Proceedings of the Royal Society,' vol. 78, series A, 1907.

tube ceased to conduct the current. The aerolite was then heated so as to expel the occluded gases, the pump set going, and the spectrum of the gas examined at various pressures down to about 20 mm.—when the pumping was stopped.

The calcium tube B was now strongly heated with a "Meker" burner: at first the gauge was depressed owing to gas liberated by the heat, and then absorption suddenly took place, and the gauge ran up to one or two millimetres or less. The spectrum was kept under examination the whole time, and for convenience the spectrum given by helium was thrown on to the eye-piece by means of a right-angled prism, so that any indication of D<sub>3</sub>, however faint, could be instantly observed.

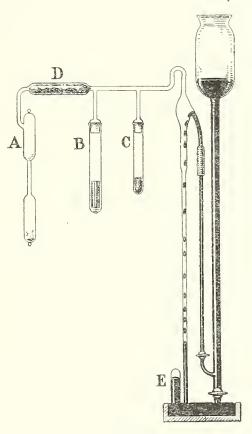


Fig. 4.

Working in this way no indication whatever was found of the lines of any of the inert gases. The absorption in each case could be carried until the tube refused to conduct the current. The final lines observed before the tube ceased to be luminous were those of mercury—generally accompanied by a faint trace of the red line of hydrogen.

In each aerolite examination—after having satisfied myself of the absence of unabsorbable gases—a further quantity of gas was driven out by heat and the pressure adjusted to about 2 mm., the vacuum tube being sealed off at this pressure and kept with full particulars of its source for future reference.

The amount of gas that could be driven out of the aerolites by heat varied considerably. In some cases it was possible to expel several successive volumes of gas and each time to repeat the absorption by calcium; in other cases the amount

of occluded gases was much less, but in all cases the calcium absorption was done at least twice, so that a very minute percentage of the inert gases would have been rendered visible.

When all the aerolites had been examined a final experiment was made to prove the efficiency of the method. A little samarskite was powdered and treated in the same way. On absorbing the liberated gases by heating the calcium—as soon as the pressure had been reduced to a few millimetres—the complete spectrum of helium was revealed.

The only gases recognised were the compounds of carbon hydrogen, and in one or two cases only H<sub>2</sub>S; this latter is somewhat remarkable, as at the time its spectrum appeared to be novel; the other aerolites were most carefully examined for it without success.

It was found impossible to get an induction spark to pass between two fragments of an aerolite, so attempts were made to make use of an arc. A fragment of the

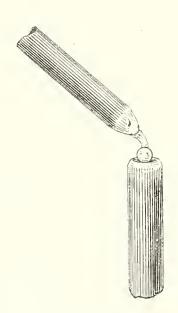


Fig. 5.

stone was ignited in a cup hollowed out of the lower carbon pole—the upper electrode being a carbon rod. As shown in fig. 5, if an arc was struck between the two carbons by momentary contact with a third rod of carbon, the fragment of stone quickly became hot and ultimately fused and formed a molten sphere; the arc could then be maintained between this sphere and the upper carbon. Photographs were obtained of the resulting arc and the spectra of several of the meteoric stones examined. The plan followed was to arrange three stops or apertures that could be adjusted in front of the slit, and by their aid to project upon the photographic film, first the spectrum given by iron; then the spectrum of the aerolite ignited between two poles of carbon; and below that the spectrum given by carbon poles alone. In this way it was easy to observe any lines in the aerolite

spectrum that did not appear in either the iron or the carbon, and thus the composition could be determined. This method was not altogether satisfactory owing to impurities in the carbon rods and the consequent uncertainty of some of the observed lines being due to constituents of the aerolite or to impurities in the carbon. I therefore tried other means.

The aerolite was finely powdered and mixed with a metallic powder, the composition of which was known. The mixture was strongly compressed in a hydraulic press, and from the solid mass thus obtained a pair of poles were fashioned.

Iron was one of the first metals used for experiment, but was discarded owing to the fact that iron is a plentiful constituent of stony meteorites. Silver was finally chosen because of the comparative ease of getting it pure—also because the lines in any part of its arc spectrum are few in comparison with the lines of iron which are exceedingly numerous all along the spectrum. Moreover, the softness of silver makes it easy to get strongly coherent poles from its mixture with the aerolite. The silver powder I used was specially prepared by a method given to me by Dr. A. Scott, F.R.S. The purest commercial silver was dissolved in nitric acid, the solution evaporated to dryness in a silica crucible, and the solid residue fused till any copper nitrate which might be present was decomposed. The mass was extracted with water, and the filtered solution of silver nitrate precipitated by means of a boiling solution of ammonium formate and acetate into which the silver solution was slowly run. After the liquid had become brilliantly clear and the silver well agglomerated, the metal was thoroughly washed and dried. The aerolite in fine powder was mixed with an equal weight of the silver, and the mixture slightly damped and compressed into a block in a hydraulic press at a pressure of 250 atmospheres. The resulting cake—after drying—was raised to dull redness, and was then cut across to form two poles between which to form the electric arc. The poles were mounted in special clips in a mechanical arrangement to enable the arc to be accurately focussed on the slit and kept there during the exposure.

## The Arc Spectrum of an Aerolite.

In order to identify the different elements present I have worked by a method unlike that adopted by most observers. Instead of measuring the wave-lengths of the lines and establishing their identity by reference to published tables of wavelengths, I have made it a rule to obtain, first, a qualitative idea of the constituents present, then to photograph the spectrum of the aerolite and silver mixture in juxtaposition with that of each suspected element by a device already described. In this way I have been able with certainty to identify every line in the spectrum of each aerolite examined. This removes the uncertainty due to irregularities in the determination of wave-lengths by different observers. I can take no responsibility for the accuracy of the figures by which I identify these lines; they are copied from the most recent and trustworthy sources—had it been possible to reproduce the actual photographed spectra that I am now exhibiting there would have been no need to have printed any figures at all. The spectrum of the aerolite is easily distinguished from the mixed silver and aerolite spectrum by reference to a photograph of the silver taken separately.

The advantage of my method becomes apparent if—for illustration—I take one element—nickel—common to all meteorites. In the range of my instrument there are no less than three hundred and forty strong lines which I have identified, and on the aerolite spectrum I have marked all the nickel lines that can be seen, together with the wave-length given in the most recent determination—but the *point* is that any line marked is actually present as found by reference to the spectrum of pure nickel, and does not rest upon a coincidence of figures.

Examination of the Arc Spectra of Thirty Aerolites.

List of aerolites thus far examined:—

## L'Aigle (from Orne, France).

The photographed spectrum of this aerolite extends from  $\lambda$  2973 to  $\lambda$  5896, and includes in addition to the lines of iron 2 aluminium, 1 calcium, 23 chromium, 3 magnesium, 3 manganese. 27 nickel, 2 potassium, 6 sodium.

## Alfianello (from Brescia, Italy).

The photographed spectrum extends from  $\lambda$  3018 to  $\lambda$  6643, and includes in addition to the lines of iron 1 aluminium, 2 calcium, 23 chromium, 2 magnesium, 3 manganese, 40 nickel, 6 sodium.

## Aubres (from Nyons, Drôme, France).

There was great difficulty in maintaining the arc. The photographed spectrum extends from  $\lambda$  2507 to  $\lambda$  5896, and contains in addition to the lines of iron 10 chromium, 6 magnesium, 3 manganese, 6 nickel, 4 silicon, 2 sodium.

## Baroti (from Bilaspur, Simla, Punjab, India).

The photographed spectrum extends from  $\lambda$  2851 to  $\lambda$  5896, and shows in addition to the lines of iron 2 aluminium, 2 calcium, 25 chromium, 2 magnesium, 3 manganese, 2 potassium, 4 sodium, 38 nickel.

# Barratta (from Deniliquin, New South Wales).

The photographed spectrum of this aerolite extends from  $\lambda$  2853 to  $\lambda$  5206, and shows in addition to the lines of iron 2 aluminium, 2 calcium. 26 chromium, 3 magnesium, 3 manganese, 29 nickel, 2 sodium.

# Bustee (from India).

This aerolite behaves in a very similar way to El Nakhla el Baharia, and it was only possible to obtain one photograph. Very few lines were found, and these were chiefly those due to chromium and magnesium; the lines of nickel cannot be seen. In addition to the lines of iron the following were identified between  $\lambda$  2852 and  $\lambda$  4289, 2 calcium, 10 chromium, 6 magnesium, 3 manganese, 2 sodium.

# Chandakapur (from Berar, India).

This is a very rare aerolite, and as I had only 2.184 grm. of the material very great care had to be taken in obtaining the spectrum.

The photographed spectrum extends from  $\lambda$  2507 to  $\lambda$  6643, and contains in addition to the lines of iron 1 aluminium, 3 calcium, 36 chromium, 7 magnesium, 3 manganese, 43 nickel, 6 silicon, 6 sodium.

# Chantonnay (from Vendée, France).

The photographed spectrum of this aerolite commences at  $\lambda$  2551 and extends to  $\lambda$  5896, and contains in addition to the lines of iron 2 aluminium,

1 calcium, 18 chromium, 2 magnesium, 3 manganese, 27 nickel, 2 potassium. 6 sodium.

#### Chateau-Renard (from Triguères, Loiret, France).

The photographed spectrum of this aerolite extends from  $\lambda$  3230 to  $\lambda$  5896, and includes in addition to the lines of iron 2 calcium, 28 chromium. 2 magnesium, 3 manganese, 44 nickel, 2 potassium, 6 sodium.

#### Crumlin (from County Antrim, Ireland).

The quantity of material in this case was small, the lines in the photographed spectrum extend from  $\lambda$  2967 to  $\lambda$  5896, and includes in addition to the lines of iron 2 aluminium, 31 chromium, 2 magnesium, 3 manganese, 38 nickel, 6 sodium.

## Dandapur (from Goruckpur, North-West Provinces, India).

The photographed spectrum of this aerolite commences at  $\lambda$  3002 and extends to  $\lambda$  5896, and includes in addition to the lines of iron 1 calcium, 24 chromium, 2 magnesium, 3 manganese, 47 nickel, 2 potassium, 4 sodium.

## Daniel's Kuil (from Griqualand East, South Africa).

The photographed spectrum of this aerolite commences at  $\lambda$  2788 and ends at  $\lambda$  6634, and includes in addition to the lines of iron 1 aluminium, 30 chromium, 3 magnesium, 3 magnese. 49 nickel, 6 sodium.

# Dhurmsala (from Kangra, Punjab, India).

The whole of the material available, 5 grm., was used and the photographed spectrum extended from  $\lambda$  2795 to  $\lambda$  6643, and includes in addition to the lines of iron 2 calcium, 28 chromium, 5 magnesium, 3 manganese, 38 nickel, 2 potassium, 6 sodium.

## Durala (from Kurnal, Punjab, India).

The photographed spectrum of this aerolite extends from  $\lambda$  2975 to  $\lambda$  5896, and includes in addition to the lines of iron 2 calcium, 19 chromium, 4 magnesium, 3 manganese, 37 nickel, 2 potassium, 4 sodium.

# Eli Elwah (Hay, Waradgery County, New South Wales).

The photographed spectrum extends from  $\lambda$  3246 to  $\lambda$  4957, and includes in addition to the lines of iron 7 chromium, 2 magnesium, 3 manganese, 27 nickel, 2 sodium.

# El Nakhla el Baharia (from Alexandria, Egypt).

This very soft stone when mixed with silver powder and compressed into a block proved to be very fusible and the arc could only be maintained for a few seconds, three short exposures only were obtained, and these were not sufficient to bring out the nickel lines.

The photographed spectrum extends from  $\lambda$  3466 to  $\lambda$  5896, and includes in

addition to the lines of iron 9 chromium, 2 magnesium. 3 manganese, 2 potassium, 4 sodium.

# Futtehpur (from North-West Provinces, India).

The photographed spectrum extends from  $\lambda$  2852 to  $\lambda$  5896, and includes in addition to the lines of iron 2 aluminium, 3 calcium, 31 chromium, 4 magnesium, 3 manganese, 48 nickel, 2 potassium, 4 sodium.

# Gilgoin (from Brewarrina, Clyde County, New South Wales).

The lines shown in the photographed spectrum of this aerolite extend from  $\lambda 2598$  to  $\lambda 5896$ , and includes in addition to the lines of iron 3 calcium, 24 chromium, 6 magnesium, 3 manganese, 37 nickel, 2 potassium, 6 sodium.

# Girgenti (from Sicily).

The photographed spectrum extends from  $\lambda 2852^{\circ}2$  to  $\lambda 5896$ , and includes in addition to the lines of iron 2 aluminium, 2 calcium, 25 chromium, magnesium, 3 manganese, nickel, 2 potassium, 4 sodium.

## Gnarrenburg (from Hanover, Prussia).

The photographed spectrum of this aerolite extends from  $\lambda 2714$  to  $\lambda 5896$ , and includes in addition to the lines of iron 2 aluminium, 3 calcium, 31 chromium, magnesium, 3 manganese, 50 nickel, 2 potassium, 6 sodium.

## Hvittis (from Abo, Finland).

The photographed spectrum of this aerolite commences at  $\lambda$  2852 and extends to  $\lambda$  5896; it includes in addition to the lines of iron 1 calcium, 30 chromium, 3 magnesium, 3 manganese, 31 nickel, 4 sodium.

# Jelica (from Servia).

The photographed spectrum of this aerolite commences at  $\lambda 2852$  and extends to  $\lambda 5896$ , and includes in addition to the lines of iron 1 calcium, 29 chromium, 3 magnesium, 3 manganese, 34 nickel, 2 potassium, 4 sodium.

# Jhung (from Punjab, India).

The lines shown in the photographed spectra extend from  $\lambda$  2883 to  $\lambda$  5896, and includes in addition to the lines of iron 2 aluminium, 2 calcium, 22 chromium, 3 magnesium, 3 manganese, 43 nickel, 2 potassium, 6 sodium.

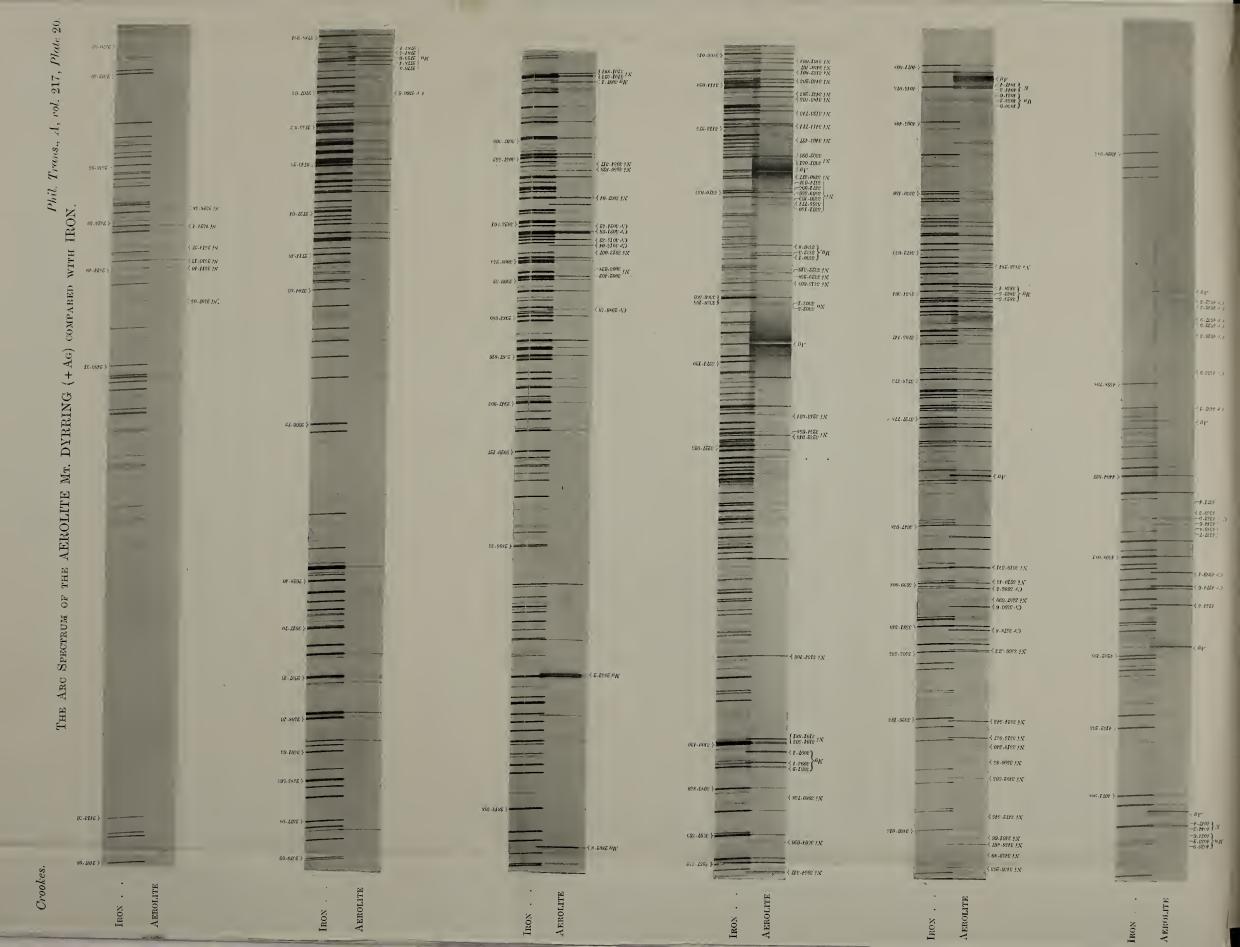
# Kansada (from Ness County, Kansas, U.S.A.).

The photographed spectrum of this aerolite commences at  $\lambda 2852$  and extends to  $\lambda 4652$ , and includes in addition to the lines of iron 1 calcium. 26 chromium, 1 magnesium, 3 manganese, 45 nickel, 4 sodium.

# Khairpur (from India). (See Plate 19.)

The photographed spectrum of this aerolite commences at  $\lambda$  2852 and ends at  $\lambda$  5896, and includes in addition to the lines of iron 2 aluminium, 3 calcium, 29 chromium, 4 magnesium, 3 manganese, 41 nickel 2 potassium, 6 sodium.





Launton (from Bicester, Oxfordshire).

The whole of the 5 grm. of material available quickly burnt out and only short exposures were possible. The photographed spectrum extended from  $\lambda$  3302 to  $\lambda$  5896, and includes in addition to the lines of iron 2 aluminium, 2 calcium, 21 chromium, 2 magnesium, 3 manganese, 20 nickel, 2 potassium, 6 sodium.

Mount Brown (from Evelyn County, New South Wales).

The photographed spectrum of this aerolite extends from  $\lambda$  2599 to  $\lambda$  6643, and includes in addition to the lines of iron 3 aluminium, 3 calcium, 28 chromium, 11 magnesium, 3 manganese, 55 nickel, 6 sodium.

Mount Dyrring (from Durham County, New South Wales). (See Plate 20.)

The lines found in the photographed spectrum of this aerolite extends from  $\lambda$  2482 to  $\lambda$  4652, and includes in addition to the lines of iron 25 chromium, 17 magnesium, 3 manganese, nickel, 2 potassium, 6 silicon, 2 sodium.

Nammianthal (from South Arcot, Madras, India).

The photographed spectrum of this aerolite extends from  $\lambda$  2716 to  $\lambda$  4652, and includes in addition to the lines of iron 2 calcium, 23 chromium, 3 magnesium, 3 magnese, 50 nickel, 2 sodium.

Parnallee (from Madras, India).

The photographed spectrum extends from  $\lambda 2788$  to  $\lambda 5896$ , and includes in addition to the lines of iron 1 aluminium, 24 chromium, 3 magnesium, 3 manganese, 50 nickel, 2 potassium, 6 sodium.

Before discussing in detail the composition of these aerolites as revealed by their arc spectra it is well to record one or two points of general importance. Keeping the current and voltage constant the number of lines recorded in the arc spectrum of a compound substance depends in large measure upon the time-length of the "exposure" and the sensitiveness of the photographic plate. For instance, if in an exposure of say five minutes there are a mass of lines, having some that are very much over-exposed and some that are only just visible, by making another exposure of the same material for double the time the very faint lines would appear stronger, and others that in the shorter exposure were not visible would come into view, and so on. But in practice a limit is fixed, governed partly by the demands of the strong lines and partly by the amount of the material at one's disposal. This latter limitation, the amount of material available, is very potent when dealing with such substances as rare meteoric stones.

From an examination of the whole set of aerolite spectra it appears that the proportion of nickel to iron is generally constant. There is a nickel line at  $\lambda$  3619'391 and an iron at  $\lambda$  3618'919; these two lines form a close pair, and in twenty-seven out of the thirty spectra they remain in the same relative intensity,

being faint or strong according to the general character of the spectrum. But in three, Bustee, El Nakhla, and Aubres, while the iron line shows as usual, the nickel line is either absent altogether or very faint.\*

In several of the aerolites in my list, it will be seen that the total number of lines recorded is below the average. The aerolite Bustee is an instance.† The rapidity with which it burnt away in the arc prevented me from giving the length of time for each exposure necessary to bring out many of the fainter lines. A rather interesting point came out in connection with this aerolite.

In the early work my stock of material amounted only to about 2 grm.—and the length of time given for an exposure was necessarily short—it was noticed that although the stronger chromium lines came out in good intensity, the nickel lines were absent. Having obtained more material I was able to get photographs with longer exposures; the nickel lines could then be seen, although as a whole much more faintly than those due to chromium. This gave rise to some experiments upon the relative photographic intensity of the two metals under the conditions in which I was working.

The chromium spectrum is fairly rich in lines. Under the conditions prevailing in these experiments, in addition to a large number of faint lines there are recorded about one hundred strong ones, and of these there are three groups, which might be called the dominant lines of the element; the strongest of these groups is composed of the three lines at  $\lambda$  4254·50,  $\lambda$  4274·97, and  $\lambda$  4289·90; the next strong group is also three lines at  $\lambda$  3578·840.  $\lambda$  3593·633, and  $\lambda$  3605·478, and the faintest consists of two lines,  $\lambda$  4862·02 and  $\lambda$  4870·9.

Some pure chromium was taken and reduced to powder, some pure electrolytic nickel was prepared in the same way, and a mixture was made of silver, kaolin, and yttria, with 10 per cent. each of Ni and Cr. This was pressed into a button and the spectrum taken as in the case of the aerolite: it was at once seen that the chromium groups came out in greater intensity than the adjacent nickel lines.

The mixture above referred to is the outcome of many experiments made to find a material capable of carrying small percentages of nickel and chromium, so that when mixed with silver and formed into electrodes for the arc it should behave in a way similar to an aerolite; the yttria was only used as a diluent of known composition.‡

An extensive series of experiments was carried out to throw light upon the

- \* In connection with this proportionality between the lines of iron and nickel, I have examined the spectra of a number of siderites, and in the majority of instances the proportionality remains constant; but there are a few cases in which the nickel line is fainter than that of iron and others in which it is stronger.
- † Through the kindness of the Trustees of the British Museum and of Dr. Prior, three successive portions of this aerolite, making 12:171 grm. in all, were placed at my disposal.
- ‡ Incidentally, I may say that this is a very convenient method for obtaining the arc spectra of the rare earths.

photographic effect of known percentages of chromium under the conditions obtaining in the aerolite spectra.

Two electrodes were made as follows:—

Nickel												
Chromiu	m	•	٠	•	٠	•	•	٠	•	٠	•	5
												100

And to this was added an equal weight of pure silver powder. The arc spectrum was then photographed under conditions similar to those of the aerolites.

It was seen that the chromium groups were still the most prominent lines in the spectrum, those of nickel being comparatively faint.

Keeping the other ingredients constant and gradually reducing the proportion of chromium several more experiments were made, and it was found that when the chromium had been so reduced that it was only 0.16 per cent., the lines  $\lambda$  4862.02 and  $\lambda$  4870.9 were no longer visible; a further experiment with electrodes containing only 0.1 per cent. chromium distinctly showed the other two groups.

These experiments show that it is easy to detect the presence of chromium in an arc between electrodes that contain only 5 parts Cr in 10,000.

It is not easy to see why in subjecting the two elements nickel and chromium to the heat of the electric arc it should produce so much more intense atomic disturbance in one case than in the other—the melting-points of the two elements are not very different—it may be, however, that the volatilisation points differ. I have pursued this matter in connection with the examination of a large number of meteoric irons (siderites) that will form the subject of a further communication.\*

Although these experiments only make it possible to form an approximate estimate of the amount of chromium present in these aerolites it would seem to lie between 0.6 per cent. and 0.1 per cent.

In the previous experiments the proportion of nickel which was kept the same in all mixtures was evidently in considerable excess of that contained in any of the

\* Without anticipating this communication on siderites, I desire to point out the remarkable fact that although the chromium lines appear, sometimes very strongly, in all my aerolite spectra they do not appear in any of the siderites I have so far examined—except in one instance, that of "Zacatecas." Although of course the nickel lines are always visible—from the spectroscopic examination of a number of specimens of iron, to which I had added decreasing amounts of chromium, I found that the dominant lines of chromium were quite visible even when the amount present was no more than 0.0175 per cent. This is due to the fact that chromium is absent from the nickel-irons but almost universally present in the aerolites in the form of chromite. In Aubres, &c., there is probably more chromite than nickel-iron. In the magma which produced meteorites all the Cr was converted into oxide or sulphide, giving rise to the mineral chromite or daubreelite and leaving no Cr for the nickel-iron.

aerolites; the experiments were therefore continued, blocks made in the same way as in the experiments with chromium were used as electrodes for the arc. The proportion of nickel was from 2 per cent. down to 0.04 per cent.—photographs of the spectrum were made under the usual working conditions. The portion of the spectrum taken was that containing the chromium group,  $\lambda$  3578.840,  $\lambda$  3593.633.  $\lambda$  3605.478, and the closely adjacent nickel lines: it was found that when the amount of nickel was reduced to 0.04 per cent, the line 3619.391 was only just visible.

The information gained from these mixtures of chromium and of nickel made it possible to obtain an approximate estimate of the quantities of these elements present in the three aerolites, El Nakhla, Aubres, and Bustee. A mixture containing chromium 0.25 per cent. and nickel 0.04 per cent. gave a photograph which for Cr-Ni was practically identical with that of Aubres.

The estimation made in this way cannot be more than a "good approximation" on account of unavoidable variations, due to intensity of light and time of exposure; also to conditions of photographic development, which cannot be exactly controlled, but the indications given by the relative intensities of closely adjacent Ni and Cr lines when they occur on the same film are very much more exact, and the result proves that in these aerolites the element chromium exists in greater abundance than nickel.

To this fact must be added that of the almost total absence of chronium in the familiar nickeliferous irons of the siderites.

In a general survey of the spectrum analyses of the 30 aerolites which forms the subject of this Paper, the most striking fact is their similarity in composition, and the small number of elements represented. Making full allowance for wide differences in the photographic activity of the arc spectra of the elements, it is remarkable that we only see with certainty the lines due to some *ten* bodies, and of these ten, four only—iron, chromium, magnesium, and nickel—appear to be present in quantity. With three exceptions, Bustee, El Nakhla, and Aubres, the proportion between these elements appears to be practically the same in all.

This suggests that these earthy meteorites must have a common origin, and that origin might be due to the disruption of a body in which the process of cosmial evolution has been completed; in short, may we not conclude that the aerolites are fragments of a finished and cooled planet. It is possible that we have in our museums fragments of a world unrealised—a world that at one time had its place between Jupiter and Mars in our planetary system.

From the results of my unfinished notes on the spectrum analyses of meteoric irons, to which I have already referred, it would appear that either the siderites are of a different origin, or that they have constituted the solid nucleus or core, from which by some process at present unknown the chromium and other elements had been separated, leaving the magnetic elements iron and nickel as the familiar ferro-nickel meteorites.

	Intensity.	L'Aigle.	Alfianello.	Aubres.	Baroti.	Barratta.	Bustee,	Chandakapur.	Chantonnay.	Chateau-Renard.	Crumlin.	Dandapur.	Daniel's Kuil.	Dhurmsala.	Durala.	Eli Elwah.	El Nakhla el Baharia.	Futtehpur.	Gilgoin.	Girgenti.	Gnarrenburg.	Hvittis.	Jelicu.	Jhung.	Kansada.	Khairpur.	Launton.	Mount Brown.	Mount Dyrring.	Nammianthal.
Nickel.										P. V. Carrier																				
2981 · 652 3002 · 492	6 10	_	_	_	-	 +	-	+	- +	+++	  +	-   +	  -  +	  -    +	- +	_	_	+++++++++++++++++++++++++++++++++++++++	- +	+	+ +	+++	- +	_ +	- +	+++++++++++++++++++++++++++++++++++++++	_	+	+	++
3003.628	9	-	-	-	_	+	-	+	+	+	+	+	+	+	+	_	-	+	+	+	+	+	+	+	+	+	-	+	+	+
$3012 \cdot 007 \\ 3037 \cdot 940$	9					++	-	+++	+	++	+++++++++++++++++++++++++++++++++++++++	++	+++++++++++++++++++++++++++++++++++++++	++	+		_	+ +	+ +	+ +	+	+	_	+ +	++	++	_	+	+	++
$3050 \cdot 828$	10				_	+	-	+	+	+	+	_	+	+	+		_	+	+	+	+	+	+	+	+	+	_	+	+	+
$3054 \cdot 317$	8	-	_	_	+	+	-	+	-	+	+	+	+	+	+	-	-	+	+	+	+	+	+	+	+	+	-	+	+	+
$3064 \cdot 626 \\ 3080 \cdot 758$	6		_	_	_	+	-	-	-	+		_	_	_	-	_				+		+	_	_	+	1	_	+ +		+
3101.563	8		+	-	+	+	_	_	_	+	+	+	+	+	_		_	+		+	+	++	+	+	+	+	_	+	+	++
3101.881	8	-	+	_	+	-	_	_	-	_	+	+	+	+	_	-	_	+		+	+	_	+	+	+	-	-	+	+	+
3134·106 3197·121	10	-	+	-	-	-	-	+	-	-	+	+	+	+	+	-	_	+	-	+	+	-	+	-	+	-	-	+	+	+
3221.661	+	_		_			_	_		_		_				_	_	_		_		_		Ξ.	+ +		_	_		
3225.030	5	-	-	_	-	-	_	_	_	_	_	_	-	_	_	_	-	-	-	-	-	-	-1	-	+	-	-	+	+	-
3232 · 945	8	-	+	+	+	-	-	+		+	+	+	+	-	_	-	-	+	-	+	+	-	+	+	+	-	-	+	+	+
3234·658 3243·064	5 8		+		+++++++++++++++++++++++++++++++++++++++			++		+	_	+	+			_	_	+		+	+ +		+	+	++		_	++	+	++
3315.668	7	-	+	-	+	_	_	+	_	+	_	+	+	+	+	-	-	+	+	+	+	_	+	+	+	+	-	+	+	+
3320 · 259	5	-	+	-	+	_	_	_	-	-	_	+	_	-	+	-	-	+	-	+	+	-	+	+	+	+	-	+	+	+
$3322 \cdot 316 \\ 3361 \cdot 550$	5 5	_	+		+	_	_	+	_	+	_	++	+	+	++	_	_	+ + +	+	+	+	+	+	+	++	+	_	+ +	+	++
$3365 \cdot 771$	4	-	+	-	+	_	-	+	_	+	-	+	+	+	+	+	-	+	+	+	+	_ '	+	+	+	+	-	+	+	+
3366 · 169	5	-	+	-	+	_	-	+	-	+	+	+	+	+	+	+	-	+			+		+	+	+	+	_	+	+	+
$3369 \cdot 576 \\ 3371 \cdot 995$	10 5	+	++	+	+	+	_	+	+	+++	+	++	+	+	++	+		+ +	+	+	+	+ +	+	+ +	+	+		+ +	<del> </del>	++
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+ means present, - means absent.

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+ means present, - means absent.

	Intensity.	L'Aigle.	Alfianello.	Aubres.	Baroti.	Barratta.	Bustce.	Cbandakapur.	Chantonnay.	Chateau-Renard.	Crumlin.	Dandapur.	Daniel's Kuil.	Dhurmsala.	Durala.	Eli Elwah.	El Nakhla el Baharia.	Futtehpur.	Gilgoin.	Girgenti.	Gnarrenburg.	Hvittis.	Jelica.	Jhung.	Kansada.	Khairpur.	Launton.	Mount Brown.	Mount Dyrring.	Nammianthal.	Parnalloe.
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