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AND

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38

CONDUCTED BY

JOHN JOLY, M.A. D.Sc. F.R.S. F.G.S.

AND

WILLIAM FRANCIS, F.L.S.

"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." Just. Lips. Polit. lib. i. cap. 1. Not.

VOL. XV.—SIXTH SERIES.
JANUARY—JUNE 1908.

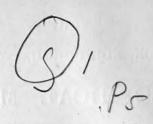


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. "Meditationis est perscrutari occulta; contemplationis est admirari perspicua . . . . Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—Hugo de S. Victore.

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

J. B. Pinelli ad Mazonium.





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MULLARY THE

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[SIXTH SERIES.]

## JANUARY 1908.

I. The Relation of Mass to Energy. By DANIEL F. COMSTOCK. Ph.D., Instructor in Theoretical Physics, Mass. Institute of Technology, Boston\*.

THETHER the inertia of matter has or has not a complete electromagnetic explanation is a question that it will perhaps take many years to answer with any degree of certainty. The experiments of Kaufmann seem to prove that in the case of a single electron the mass is entirely of this origin; and it is impossible therefore to avoid the conclusion that at least a fraction of ordinary material inertia is also electromagnetic. Doubtless there is a psychological cause for our reluctance to accept the electromagnetic explanation as complete, constant familiarity with ponderable bodies having blinded us to the possibility of anything being more fundamental; but certain it is, that if we free ourselves from prejudice as much as possible and adopt the well-tried policy of choosing the simplest theory which adequately represents the phenomena,—the theory that is, which involves the least number of variables,-we must decide in favour of the complete electromagnetic explanation, which involves only the æther and its properties.

2. The complexity of the Zeeman effect and the relations

<sup>\*</sup> Communicated by the Author.

between the wave-lengths of the spectral lines, make it seem probable that if matter is to be considered as an electrical system, it must be much more complex than a system composed entirely of electrons separated by distances great in comparison to their size. It becomes therefore of interest to see whether any relations can be found between the mass of an electric system in general, and any of its other properties. It will be found that a general relation does exist, which is not only of considerable interest in itself, but also suggests other relations.

3. The straightforward calculation of the mass of an electric system possessing any distribution of charge and any internal velocities below that of light presents considerable difficulty; for such calculation involves the use of the scalar and vector potential, and these are not effective instantaneously at all parts of the system. Any expression for the mass of the system calculated in this way will therefore involve terms which vary in an extremely complicated way with the internal velocities when these are not very small. The same is true with respect to the velocity of the system as a whole. In the following discussion the problem is attacked in an entirely different way, which is not open to this objection.

As the constraints of the system are intimately involved,

it will be well first to consider them.

4. The position of internal constraints in general electrical theory is a very fundamental one. By "constraints" are meant rigid connexions of any kind. These act merely as reactions to the electrical forces, and do not contribute to the virtual work. If the electrical laws are to hold universally, i. e., for minute distances as well as for greater ones, it is obvious that no electrical system can exist as such unless there are such constraints to balance the electrical forces. Even a single electron would dissipate itself through the mutual repulsion of its elements, were it not for some form of internal constraint. Besides holding the system together, as it were, these constraints also act in another important way. They may become, in common with all geometrical constraints, paths of energy We are accustomed to think of the Poynting vector as representing completely the energy flow in a purely electrical system, but of course this is not in general true.

Take as a simple example the case of a large plane aircondenser moving in a direction perpendicular to the plane of its plates. If the condenser is charged there is obviously a transference of energy at a rate equal to the internal energy multiplied by the velocity of movement. The Poynting vector is, however, zero. The energy transfer is not through space in the ordinary sense, but is along the constraint which holds the condenser-plates apart. The plate in the rear picks up, as we may say, the energy of the field, and after it has been transmitted to the forward plate by means of the constraint it is there set down again. On the other hand, when the condenser is moving parallel to the plane of the plates, there is no energy flow along the constraint and the Poynting vector adequately represents the transfer of energy. So also in the case of a single moving electron, the rate of transfer of energy is not given by the integration of the Poynting vector through all space, but differs from this by an amount corresponding to the energy-flow along the constraints in the body of the electron. This does not mean that there is any energy associated with the constraints, for of course rigid constraints can neither absorb nor give out energy; there is no storing up, but merely a transfer.

5. It is not difficult to find an expression for this rate of transfer. If the constraint is a simple linear one the transfer of energy along its direction is evidently

### -lTv'

where (l) is the length of the constraint, (v') the velocity with which it is moving along its length, and (T) the tension along it. The amount of energy (Tv') per sec. is put at the forward end, and is instantly available at the rear end at a distance (l). If the velocity (v) makes an angle  $(\theta)$  with the constraint,  $v'=v\cos\theta$ , and the transfer in the direction of v is

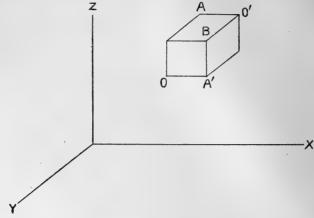
## $-lTv\cos^2\theta$ .

Another type of transfer enters when there is shearing stress in the constraint, a transfer that is which is in a direction perpendicular to that of velocity. It must be remembered that the constraints are described in no way except geometrically.

If we consider therefore the general case where the stress in the body of the constraint is represented mathematically by the nine stresses commonly used in the theory of elasticity, namely,  $X_z$ ,  $Y_z$ ,  $Z_z$ ,  $X_z$ ,  $Y_y$ ,  $Z_y$ ,  $Z_z$ ,  $Z_z$ , then there is a rate of transfer of energy in the x-direction through unit volume given by

$$f_x' = -(v_x + X_x v_y Y_x + v_z Z_x).$$

This can be readily shown by a consideration of the figure. When the velocity of the element is along (x) there is an



amount of work  $(v_x.X_x)$  dy.dz done per second on the element by the tension  $(X_x)$  applied at the surface (O'A'), and this energy is instantly available at the surface (OA), where it is given out. The distance over which the energy is transmitted being dx (the thickness of the element), the rate of energy-flow is

$$-v_x X_x dy dz dx = -v_x X_x d\tau,$$

where  $(d\tau)$  is the element of volume.

In like manner the velocity  $(v_y)$  and the shearing stress  $(Y_x \cdot dy \cdot dz)$  cause energy to be taken up at the surface (O'A') and given out at the surface (OA), and we have the rate of flow along the x-axis

 $-v_{y}Y_{x}d\tau$ ;

and finally the velocity  $(v_z)$  and the shearing stress  $(Z_x, dy, dz)$  give

 $-v_z \mathbf{Z}_x d\tau$ .

Hence adding we have, if we call  $(f_x')$  the density of flow along x,

 $f_x'd\tau = -(v_x \mathbf{X}_x + v_y \mathbf{Y}_x + v_z \mathbf{Z}_x) d\tau.$ 

Obtaining the corresponding equations in similar way we have finally for the three components of the density of energy-flow along the constraints in any system

$$f_{x}' = -(v_{x}X_{x} + v_{y}Y_{x} + v_{z}Z_{x}),$$

$$f_{y}' = -(v_{x}X_{y} + v_{y}Y_{y} + v_{z}Z_{y}),$$

$$f_{z}' = -(v_{x}X_{z} + v_{y}Y_{z} + v_{z}Z_{z}).$$
(1)

For the total density of energy-flow  $(f_x, f_y, f_z)$  we must of course add to the above the components of the Poynting vector. Writing as usual X, Y, Z and  $\alpha$ ,  $\beta$ ,  $\gamma$  for the electric and magnetic force intensities and calling (V) the velocity of light, we have

$$f_{x} = \frac{V}{4\pi} (\gamma Y - \beta Z) - (v_{x}X_{x} + v_{y}Y_{x} + v_{z}Z_{x}),$$

$$f_{y} = \frac{V}{4\pi} (\alpha Z - \gamma X) - (v_{x}X_{y} + v_{y}Y_{y} + v_{z}Z_{y}),$$

$$f_{z} = \frac{V}{4\pi} (\beta X - \alpha Y) - (v_{x}X_{z} + v_{y}Y_{z} + v_{z}Z_{z}),$$
(2)

These equations give the density of the total energy-flow through any purely electrical system, in which the ordinary

electrical laws hold universally.

6. Consider an isolated electrical system moving as a whole through space with the constant velocity  $(v_1)$ . A constant velocity will be possible if the system retains on the average the same internal structure. The total average rate of transfer of energy corresponding to the movement of such a system is evidently  $(v_1 \cdot W)$ , where W is the total contained energy. Another expression for the same thing is to be obtained by integrating throughout the system the components along  $(v_1)$  of  $(f_x, f_y, f_z)$  given in equations (2). In order that the velocity  $(v_1)$  may appear explicitly, however, it is necessary that the velocity (v), which was used in equations (2), be written as the sum of  $(v_1)$  and another velocity  $(v_2)$ . Then  $(v_2)$  is the velocity with respect to axes moving with the system.

If l, m, n are the direction cosines of the constant velocity  $(v_1)$ , we have for the total energy-flow (F) in the direction

$$\begin{split} & V_{v_1} = \mathbf{F} = \int (lf_x + mf_y + nf_z)d\tau \\ &= \frac{lV}{4\pi} \int (\gamma \mathbf{Y} - \beta \mathbf{Z})d\tau - lv_1 \int (l\mathbf{X}_x + m\mathbf{Y}_x + n\mathbf{Z}_x)d\tau - l \int (v_{2x}\mathbf{X}_x + v_{2y}\mathbf{Y}_x + v_{2z}\mathbf{Z}_x)d\tau \\ &+ \frac{mV}{4\pi} \int (\alpha \mathbf{Z} - \gamma \mathbf{X})d\tau - mv_1 \int (l\mathbf{X}_y + m\mathbf{Y}_y + n\mathbf{Z}_y)d\tau - m \int (v_{2x}\mathbf{X}_y + v_{2y}\mathbf{Y}_y + v_{2z}\mathbf{Z}_y)d\tau \\ &+ \frac{nV}{4\pi} \int (\beta \mathbf{X} - \alpha \mathbf{Y})d\tau - nv_1 \int (l\mathbf{X}_z + m\mathbf{Y}_z + n\mathbf{Z}_z)d\tau - n \int (v_{2x}\mathbf{X}_z + v_{2y}\mathbf{Y}_z + v_{2z}\mathbf{Z}_z)d\tau \end{split}$$

Since the proof of equations (1) is equally valid for relative motion, the integrals involving  $(v_2)$  in the above correspond to flow of energy with respect to axes moving with the system. There is also an *implicitly* involved internal term in each of the Poynting vector integrals. Since the system is isolated, the sum of such "internal" terms must on the average vanish. There remains therefore to represent the actual average rate of transfer of energy through space only the explicit Poynting terms and the terms involving  $(v_1)$ .

The electromagnetic momentum corresponding to any

electrical system is given by the components

$$M_{x} = \frac{1}{4\pi V} \int (\gamma Y - \beta Z) d\tau$$

$$M_{y} = \frac{1}{4\pi V} \int (\alpha Z - \gamma X) d\tau$$

$$M_{z} = \frac{1}{4\pi V} \int (\beta X - \alpha Y) d\tau$$
(4)

which, except for the factor  $V^2$ , are the same as the integrals of the components of the Poynting vector throughout the system. Hence equation (3) may be written

$$Wv_1 = lM_x + mM_y + nM_z - lv_1 \int (lX_x + mY_x + nZ_x)d\tau$$

$$-mv_1 \int (lX_y + mY_y + nZ_y)d\tau - nv_1 \int (lX_z + mY_z + nZ_z)d\tau$$

$$(3 \text{ A})$$

Also if the electrical system here dealt with is to represent a material body, we may assume that the resultant momentum (M) is in the direction of the velocity, and hence

$$\mathbf{M} = l\mathbf{M}_x + m\mathbf{M}_y + n\mathbf{M}_z$$
.

This may be considered as due to the fact that the lack of symmetry necessarily involved in the intimate structure of any electromagnetic system has become a symmetrical average in particles large enough to be dealt with. This symmetrical point may of course have been reached in the case of single atoms. We may now write (3 A) in the form

$$Wv_1 = V^2 M - v_1 \int \{ (l^2 X_x + m^2 Y_y + n^2 Z_z) + ln(X_y + Y_x) + ln(X_z + Z_x) + mn(Y_z + Z_y) \} d\tau. \quad (5)$$

7. To reduce this expression further requires some relation to be established between the stresses and the electric and magnetic force intensities. This process is closely analogous to the derivation of the Maxwell stress in the free æther

except that we here have to deal with, besides the forces in the constraint, only the electromagnetic force on electricity embedded in the constraint, and we have nothing to do with hypothetical stresses in the free æther.

If  $(\rho)$  represents the electric density and  $(\mathscr{F}_x)$  the x-component of the total electromagnetic force on unit charge

embedded in the constraint, we have

$$\frac{\partial X_{x}}{\partial x} + \frac{\partial X_{y}}{\partial y} + \frac{\partial X_{z}}{\partial z} = -\rho \mathcal{F}_{x}$$

$$= -\rho X - \frac{\rho}{V} (v_{y} \gamma - v_{z} \beta)$$

$$= -\rho X - (k_{y} \gamma - k_{z} \beta)$$
(6)

where (k) is the density of convection current caused by the movement with velocity (v) of the electricity of density  $(\rho)$ .

Making use temporarily of the vector terminology for the sake of brevity and calling the electric force (E), the magnetic (H), and the sign [ ] denoting the vector product, we have

$$-\rho \mathscr{F}_x = -\rho \mathbf{E}_x - [k\mathbf{H}].$$

Since div E= $4\pi\rho$  and curl H  $-\frac{1}{V}\frac{\partial E}{\partial t} = 4\pi k$ ,

$$-\rho \mathscr{G}_x = -\frac{1}{4\pi} \left\{ \mathbf{E}_x \operatorname{div} \mathbf{E} + \left[ \operatorname{curl} \mathbf{H} - \frac{1}{\mathbf{V}} \frac{\partial \mathbf{E}}{\partial t}, \mathbf{H} \right]_x \right\}$$
$$= -\frac{1}{4\pi} \left\{ \mathbf{E}_x \operatorname{div} \mathbf{E} + \left[ \operatorname{curl} \mathbf{H}, \mathbf{H} \right]_x - \left[ \frac{1}{\mathbf{V}} \frac{\partial \mathbf{E}}{\partial t}, \mathbf{H} \right]_x \right\}. (7)$$

Now it is an easily verifiable identity that

 $\mathbf{E}_{x} \operatorname{div} \mathbf{E} - [\mathbf{E}, \operatorname{curl} \mathbf{E}]_{x} + \mathbf{H}_{x} \operatorname{div} \mathbf{H} + [\operatorname{curl} \mathbf{H}, \mathbf{H}]_{x}$   $= \frac{\partial}{\partial x} \{ \frac{1}{2} (\mathbf{E}_{x}^{2} - \mathbf{E}_{y}^{2} - \mathbf{E}_{z}^{2}) + \frac{1}{2} (\mathbf{H}_{x}^{2} - \mathbf{H}_{y}^{2} - \mathbf{H}_{z}^{2}) \}$   $+ \frac{\partial}{\partial x} (\mathbf{E}_{x} \mathbf{E}_{y} + \mathbf{H}_{x} \mathbf{H}_{y}) + \frac{\partial}{\partial z} (\mathbf{E}_{x} \mathbf{E}_{z} + \mathbf{H}_{x} \mathbf{H}_{z}); \quad . \quad (8)$ 

and hence, remembering that div H=0, equation (7) becomes

$$-\mathscr{F}_{x} = -\frac{1}{4\pi} \left\{ \frac{\partial}{\partial x} \left\{ \frac{1}{2} (\mathbf{E}_{x}^{2} - \mathbf{E}_{y}^{2} - \mathbf{E}_{z}^{2}) + \frac{1}{2} (\mathbf{H}_{x}^{2} - \mathbf{H}_{y}^{2} + \mathbf{H}_{z}^{2}) \right. \right.$$

$$\left. + \frac{\partial}{\partial y} (\mathbf{E}_{x} \mathbf{E}_{y} + \mathbf{H}_{x} \mathbf{H}_{y}) + \frac{\partial}{\partial z} (\mathbf{E}_{x} \mathbf{E}_{z} + \mathbf{H}_{x} \mathbf{H}_{z}) \right.$$

$$\left. + [\mathbf{E}, \text{ curl } \mathbf{E}]_{x} - \left[ \frac{1}{V} \frac{\partial \mathbf{E}}{\partial t}, \mathbf{H} \right]_{x} \right\}. \qquad (9)$$

Since

[E, curl E]<sub>x</sub> = 
$$-\left[E, \frac{1}{V} \frac{\partial H}{\partial t}, H\right]_{x}$$

the last two terms in the bracket of (9) become together

$$-\frac{1}{V^2}\frac{\partial}{\partial t}[EH]_x,$$

which is minus the time rate of the density of momentum at the point. The time rate, however, refers to a point fixed in space, and to change to a point moving with the system we make use of the usual expression and write

$$-\frac{\partial}{\partial t}m_x = -\frac{\partial'}{\partial t}m_x + v_1\left(l\frac{\partial m_x}{\partial x} + m\frac{\partial m_x}{\partial y} + n\frac{\partial m_x}{\partial z}\right), \quad (10)$$

where  $m_x$  is the x-component of the density of momentum and (l, m, n) are, as formerly, the direction cosines of the

constant velocity  $(v_1)$ . The operator  $\frac{\partial}{\partial t}$  now refers to the

rate of change at a point moving with the system.

Substituting (10) for the two last terms in (9) and noticing that

$$\frac{\partial' m_x}{\partial t}$$
 may be written  $\frac{\partial}{\partial x} \frac{\partial'}{\partial t} \int_{\mathbb{R}}^{\mathbf{r}} m_x dx$ ,

where the integration is to be taken from R (meaning merely from a point outside the system where  $m_x$  is zero) up to the point P in question, account being taken of any discontinuity at the bounding surface, we have in place of (9)

$$\frac{\partial X_{x}}{\partial x} + \frac{\partial X_{y}}{\partial y} + \frac{\partial X_{z}}{\partial z} = -\rho \mathcal{F}_{x}$$

$$= \frac{\partial}{\partial x} \left\{ -\frac{1}{8\pi} (E_{x}^{2} - E_{y}^{2} - E_{z}^{2}) - \frac{1}{8\pi} (H^{x2} - H_{y}^{2} - H_{z}^{2}) - v_{1} l m_{x} + \frac{\partial'}{\partial t} \int_{\mathbf{R}}^{\mathbf{P}} m_{x} dx \right\}$$

$$+ \frac{\partial}{\partial y} \left\{ -\frac{1}{4\pi} (E_{x} E_{y} + H_{x} H_{y}) - v_{1} m m_{x} + \frac{\partial'}{\partial t} \int_{\mathbf{R}}^{\mathbf{P}} m_{x} dy \right\}$$

$$+ \frac{\partial}{\partial z} \left\{ -\frac{1}{4\pi} (E_{x} E_{z} + H_{x} H_{z}) - v_{1} n m_{x} + \frac{\partial'}{\partial t} \int_{\mathbf{R}}^{\mathbf{P}} m_{x} dz \right\}. \qquad (11)$$

This equation gives us what we were seeking, namely, the values of  $X_z$ ,  $X_y$ , and  $X_z$  in terms of the electric and magnetic forces and the density of the momentum.

Thus we may take

$$X_{x} = -\frac{1}{8\pi} (E_{x}^{2} - E_{y}^{2} - E_{z}^{2}) - \frac{1}{8\pi} (H_{x}^{2} - H_{y}^{2} - H_{z}^{2}) - v_{1} l m_{x} + \frac{\partial'}{\partial t} \int_{R}^{P} m_{x} dx$$

$$X_{y} = -\frac{1}{4\pi} (E_{x} E_{y} + H_{x} H_{y}) - v_{1} m m_{x} + \frac{\partial'}{\partial t} \int_{R}^{P} m_{x} dy$$

$$X_{z} = -\frac{1}{4\pi} (E_{x} E_{z} + H_{x} H_{z}) - v_{1} m m_{x} + \frac{\partial'}{\partial t} \int_{R}^{P} m_{x} dz . . . . . . . . . (12)$$

Similar values are of course to be found for the other six components of stress in the constraint  $Y_x$ ,  $Y_y$ ,  $Y_z$ ,  $Z_x$ ,  $Z_y$ ,  $Z_z$ .

8. The values for these nine stress-components are now to be substituted in equation (5). In doing this it is to be noticed that the last term in each of equations (12) will, after substitution, furnish a term of the type

$$\int d\tau \frac{\partial'}{\partial t} \int_{\mathbf{R}}^{\mathbf{P}} v_1 l^2 m_x dx = \frac{\partial'}{\partial t} \int d\tau \int_{\mathbf{R}}^{\mathbf{P}} v_1 l^2 m_x dx, \quad . \quad (13)$$

and this, being a time derivative, gives an average value of zero when the time is allowed to increase indefinitely, since all quantities in the system remain finite. Also

$$l^2 + m^2 + n^2 = 1$$
.

Making the substitution in (5) and simplifying, we have as the value for  $(v_1W)$ 

$$\begin{aligned} \mathbf{v_{1}W} &= \mathbf{V}^{2}\mathbf{M} - \mathbf{v_{1}} \int \left\{ \frac{1}{8\pi} (\mathbf{E}_{x}^{2} + \mathbf{E}_{y}^{2} + \mathbf{E}_{z}^{2}) + \frac{1}{8\pi} (\mathbf{H}_{x}^{2} + \mathbf{H}_{y}^{2} + \mathbf{H}_{z}^{2}) \right\} d\tau \\ &+ v_{1} \frac{1}{4\pi} \int \left\{ (l\mathbf{E}_{x} + m\mathbf{E}_{y} + n\mathbf{E}_{z})^{2} + (l\mathbf{H}_{x} + m\mathbf{H}_{y} + n\mathbf{H}_{z})^{2} \right\} d\tau \\ &+ v_{1}^{2} \int (lm_{x} + mm_{y} + nm_{z}) d\tau. \quad . \quad (14) \end{aligned}$$

Now the first integral represents the total included energy, the two parts of the second integral represent the squares of the components of the electric and magnetic forces in the direction of the motion of the system, and the last integral represents the momentum in the direction of motion, which in this case is the whole momentum M, since we have assumed that M and  $v_1$  are in the same direction.

Calling

$$\frac{1}{8\pi}\!\int\!\left\{(l\mathbf{E}_{\boldsymbol{x}}\!+\!m\mathbf{E}_{\boldsymbol{y}}\!+\!n\mathbf{E}_{\boldsymbol{z}})^2\!+\!(l\mathbf{H}_{\boldsymbol{x}}\!+\!m\mathbf{H}_{\boldsymbol{y}}\!+\!n\mathbf{H}_{\boldsymbol{z}})^2\right\}\,d\tau\!=\!\mathbf{W}_{\mathbf{L}}$$

the longitudinal energy of the system, and

$$W - W_L = W_T$$

the transverse energy of the system, we may rewrite equation (14) as

 $v_1 W = V^2 M - v_1 W + 2v_1 W_L + v_1^2 M,$  (15)

and hence

$$\mathbf{M} = \frac{2\mathbf{W_T}v_1}{\mathbf{V}^2 \left(1 + \left\{\frac{v_1}{\mathbf{V}}\right\}^2\right)}.$$
 (16)

This gives the total momentum of any isolated, moving, purely electrical system, which has on the average the same internal structure, in terms of its transverse energy, i. e., the energy represented by the components of the electric and magnetic forces which are perpendicular to the velocity of the system. The mass of the system is then

$$\operatorname{Mass} = \frac{d\mathbf{M}}{dv_{1}} = \frac{2}{\mathbf{V}^{2}} \frac{\mathbf{W_{T}}}{\left\{1 + \left(\frac{v_{1}}{\mathbf{V}}\right)^{2}\right\}} \left\{1 - 2\left(\frac{v_{1}}{\mathbf{V}}\right)^{2} \frac{1}{\left\{1 - \left(\frac{v_{1}}{\mathbf{V}}\right)^{2}\right\}}\right\} + \frac{4\left(\frac{v_{1}}{\mathbf{V}}\right) \frac{d\mathbf{W_{T}}}{dv_{1}^{2}}}{\left\{1 + \left(\frac{v_{1}}{\mathbf{V}}\right)^{2}\right\}}$$

$$(17)$$

If, as we have assumed in deriving this expression, the system possesses the same momentum for uniform translation in any direction, this formula for the mass can contain terms of even powers only in the ratio of the velocity of the system to the velocity of light. If we neglect terms of the second and higher orders  $W_T$  has the same value as for  $v_1 = 0$ , which from symmetry of the system must be two-thirds the total energy W. Therefore

Mass = 
$$\frac{4}{3} \frac{W}{V^2}$$
, . . . . (18)

if second order terms be neglected. This formula would apply with extreme accuracy for the electromagnetic mass of ponderable bodies, for no such bodies have in nature a

velocity large enough to make  $\left(\frac{v_1}{\overline{V}}\right)^2$  appreciable.

It should be noticed that in equation (17) second order terms may enter in either  $(W_T)$  or its derivative with respect to  $v_1^2$ . In fact such terms do enter for two reasons. In the first place, the setting of the body in motion requires work and hence adds new energy, through a second order term; and secondly there is an effect due to the change which

motion causes in the velocity of propagation through the system of electrical disturbances. This is seen in the simple case of a moving electron where the crowding of the lines towards the equator with increase of velocity is only partly due to the added energy. It is evident, therefore, that for velocities so great that the second order terms cannot be neglected, the mass depends on complicated terms which vary with the internal structure and motions of the system, and it does not appear as if a general expression for the mass of a system for such high velocities could be found.

The second order terms may in the future make themselves experimentally manifest through an increase of mass of

rapidly moving  $\alpha$ -particles.

9. Expression (18) may readily be verified for simple symmetrical systems. For a single charged conducting sphere of radius (a) the mass for slow velocities is well-known to be

$$\frac{2}{3}\frac{1}{V^2}\frac{e^2}{a} = \frac{2}{3}\frac{e}{V^2}\frac{e}{a} = \frac{4}{3V^2}\frac{1}{2}(e \cdot \text{Potential}) = \frac{4}{3V^2}W.$$

An interesting verification of equation (16) for the special case of a general, rigid, electrostatic system in translatory motion has been furnished me privately by Mr. G. F. C. Searle. He obtains for such a system (Phil. Mag. Jan. 1907, p. 129) the expression

 $\mathbf{M}_{x} = \frac{2\mathbf{T}}{\mathbf{v}_{1}}, \qquad (19)$ 

where  $M_x$  is the momentum of the entire system along the direction (x) of motion, (T) is the total magnetic energy due to this motion, and  $(v_1)$  is the common translatory velocity possessed by all parts of the system.

Now it is well known that where the Faraday tubes move through space uniformly, as in the present case, the magnetic force (H) is given in terms of the electric force (E) by the

expression

$$\mathbf{H} = \frac{v_1}{\mathbf{V}} \mathbf{E} \sin \theta,$$

( $\theta$ ) representing the angle between (E) and the velocity of motion ( $v_1$ ), and (H) being in a direction perpendicular both to (E) and ( $v_1$ ). In the present notation

$$\mathbf{H} = \frac{r_1}{\mathbf{V}} \sqrt{\mathbf{E}_y^2 + \mathbf{E}_z^2},$$

and hence we have

$$T = \frac{H^2}{8\pi} = \frac{1}{8\pi} \frac{v_1^2}{\mathbf{V}^2} (\mathbf{E}_y^2 + \mathbf{E}_z^2). \qquad (20)$$

Combining (19) and (20) we can obtain

$$M_{x} = \frac{v_{1} \cdot 2\left\{\frac{1}{8\pi}(E_{y}^{2} + E_{z}^{2}) + T\right\}}{V^{2}\left(1 + \frac{v_{1}^{2}}{V^{2}}\right)}, \quad (21)$$

and remembering that

$$T = \frac{1}{8\pi} (H_y^2 + H_z^2),$$

we have finally

$$M_{x} = \frac{2W_{T}v_{1}}{V^{2}\left(1 + \frac{{v_{1}}^{2}}{V_{2}}\right)}, \quad (22)$$

which, since  $(v_1)$  is along (x), is identical with (16). Thus (16) is verified for the case where the moving system possesses no internal motion.

Perhaps the simplest symmetrical system containing magnetic as well as electric energy is that formed by a great number of charged spheres moving in straight lines out from a common centre, with velocities small enough so that the fourth and higher powers may be neglected. They are to be at distances from each other great in comparison with their size, and at equal distances from the common centre. If the system be now given the slow velocity  $(v_1)$  as a whole the total momentum accompanying this motion may be determined. Because of limited space the calculation will not be here given, but if it be carried out along established lines it

will be found that the mass is  $\frac{4}{3}\frac{1}{V^2}$  times the sum of the

electric and magnetic energies, thus verifying equation (18).

10. We conclude that, if ordinary material mass has an electromagnetic basis, such mass for slow velocities is proportional to the total electromagnetic energy-content of the body, and the laws of conservation of mass and energy become closely related if not identical. In any case the expression given represents the electromagnetic part of the total mass whatever that may be.

# Considerations suggested by the Foregoing. The Atomic Weights.

11. If the conclusion of the last article is correct a diminution in mass should follow a loss of energy in material transformations. Calculation shows, however, that in the

case of the powerful reaction between hydrogen and oxygen forming water, the change of mass would only be of the order  $10^{-10}$  gram. In the case of radioactivity, however, the energy change is very much greater and an appreciable effect is to be expected. Thus if a radium atom gives off an  $\alpha$ -particle of mass (m) with velocity  $(\mu)$ , then there should be a diminution in the sum of the masses of the  $\alpha$ -particle and the remaining atom equal to

$$\frac{4}{3}\,\frac{1}{{\bf V}^2}({\textstyle \frac{1}{2}}m\mu^2),$$

since  $\frac{1}{2}m\mu^2$  represents the energy lost, and this, calling m=4 (using gram-atomic weight) and  $\mu=2\cdot 5\cdot 10^9$ , gives

$$\Delta (\text{Mass}) = -1.7 \cdot 10^{-2} \text{ gram};$$

an amount large enough to cause discrepancies in calculating the atomic weights of radioactive substances from the number of  $\alpha$ -particles lost. Since  $\Delta$  (Mass) is proportional to the square of the velocity of the  $\alpha$ -particle, its value would be greatly increased by a slight error in the determination of

 $(\mu)$  and the effect could easily be much larger.

12. A consideration of some interest is the following. we adopt the disintegration theory, we are obliged to think of the various atoms as combinations or groups, more or less modified, of the lighter atoms. If there were perfect conservation of mass this would introduce a certain uniformity in the relations between the atomic weights, a uniformity which apparently does not exist. On the other hand, if we take into consideration the inevitable change of mass when the electromagnetic energy of the system is modified, the atomic weights will involve a correction term depending upon the change in this energy, and hence they will no longerbear simple, exact relations to each other. In a highly important paper (Zeitschrift für Anorg. Chemie, xiv. p. 66, 1897) Rydberg has shown that the atomic weights of the first twenty-seven elements of the periodic system approximate to whole numbers very much more closely than chance could bring about. He has also shown that the atomic weights of these elements are best considered as the sum of two parts (N+D) where N is an integer and D is a fraction, in general positive and smaller than unity. If M is the number of the element in the system (called by Rydberg the "Ordnungszahl"), then N is equal to 2M for the elements of even valence and 2M+1 for the elements of odd valence. Below is given a table showing the various quantities. I have used, however, the International Atomic Weight values for 1907 instead of those Rydberg used.

Sign.	М.	_	N. 2M+1	Atomic Weight.	D.	Sign.	М.	2M.	N. 2M+1	Atomic Weight.	D.
He	2	4		4		P	15		31	31.0	.0
Li	3		7	7.03	.03	S	16	32		32.06	.06
Be	4	8		9.1	1.1	Cl	17		35	35.45	.45
B	5		11	11.0	.0	A	18	36		39.9	3.9
C	6	12		12.00	.0	K	19		39	39.15	15
N	7		15	14.01	99	Ca	20	40		40.1	.1
0	8	16		16.00	.0	Sc	21		43	44.1	1.1
Fl	9		19	19.0	.0		22	44			-
Ne	10	20		20.0	.0		23		47		
Na	11		23	23.05	.05	Ti	24	48		48.1	1
Mg	12	24		24.36	.36	V	25		51	51.2	2
Al	13		27	27.1	-1	Cr	26	52		52.1	1
Si	14	28		28.4	.4	Mn	27		55	55.0	.0
						Fe	28	56		55.9	.1
										7	

The orderly arrangement of the series is striking. It will be noticed that in three cases only are the D's greater than

unity and only in two cases are they negative.

Rydberg points out that although the heavier elements do not conform well to this scheme, i. e., do not in general give the small fractional values of (D) noticed above, yet this is in reality no valid objection, for the numerical values of the weights of heavier elements depend much more on the value of the arbitrary unit chosen than do those of the lighter weight elements, and hence they can have little influence one way or the other in estimating the validity of the curious relations he sets forth.

The whole question is of course whether these differences represent real physical deviations from something or whether they are merely mathematical remainders. Rydberg certainly believes them to represent physical realities, and considering the before-mentioned overwhelming improbability that the approximation of the atomic weights to whole numbers is due to chance, we can hardly doubt that he is right.

13. Now it is to be noticed that these deviations find a ready explanation when the conclusions of the present paper are combined with the theory, so much favoured recently, that one element breaks down into two or more others with an accompanying expulsion of energy. The deviations are then to be explained as resulting from loss of mass accompanying the dissipation of energy. On the other hand, if no such loss of mass takes place, the existence of these deviations in the

table of atomic weights becomes a well-nigh insuperable difficulty in the path of the evolutionary theory of the elements.

If we follow the present suggestion, we must search for the components of an element, not by comparing atomic weights, but by comparing the corresponding values of N, for the atomic weights deviate because of the lost mass

accompanying the dissipation of internal energy.

Very recently Sir W. Ramsay has announced several striking discoveries which seem to add much weight to the disintegration theory, and, indirectly, to the views here set forth. He found helium, neon, or argon appearing as a product of radium emanation according to the exterior conditions imposed, and he found lithium appearing when a coppersulphate solution was left in the presence of the emanation. Prof. Ramsay states, I believe, that every source of error was eliminated and that the results were obtained many times.

14. It should be noticed that this theory of loss of mass and its consequences does not require that the whole material mass should be of electromagnetic nature. It only requires that the energy lost in the transformations, explosive or otherwise, should be at the expense of internal electromagnetic energy, i. e., that the forces which expel the  $\alpha$ -particles should be electric or magnetic.

## Respecting Gravitation.

15. The experiments of many investigators have shown that up to a high degree of accuracy the ratio of mass to weight for different substances is the same. Now if the mass is proportional to the internal energy as here suggested, instead of being proportional to the number of electric nuclei as might be supposed, the conclusion is apparently forced upon us that gravitational attraction is between quantities of confined energy, and not between quantities of "matter" in any other sense.

On this basis, the weight of a calorie at the earth's surface would be of order 10<sup>-11</sup> dyne. This is apparently too small to explain the temperature gradient in the earth although the calculation, depending as it does on the mechanical force on confined energy due to a temperature gradient, would certainly

depend to a large degree on the medium.

If we assume this gravitational effect, it is interesting to ask whether free energy would also show an attraction for itself. If so, the energy radiated from a gravitational centre like the sun would leave some of itself behind along its path as it moved through space, and it might be possible to account in this way for some of the energy which is ordinarily

thought of as totally dissipated.

Another conclusion which is suggested by the foregoing is that, assuming the loss of mass accompanying dissipation of energy, the sun's mass must have decreased steadily through millions of years. If too, our conclusion respecting the gravitating quality of confined energy be correct, the gravitation constant of the sun has also decreased and the distances of the planets must have increased accordingly. This last increase of planetary distance can be calculated by making the angular momentum of the planet about the sun a constant, and allowing the mass of the planet, together with the gravities of both sun and planet, to grow less with time.

So little is known as to the former radiating power of the sun that no even approximate calculation can be made, but it is not difficult to show that the order of magnitude is such as might make the increase in the planetary distances not altogether negligible during great lapses of time.

## A Proof from a different Point of View.

16. The proof of expression (17) which has been given has the advantage of entering intimately into the structure of the general system and showing the part that non-electrical forces in the form of constraints must play if the fundamental laws of electrical action are to hold for every infinitesimal element of the finite volume occupied by any electrical system. Although this is assumed in every mathematical derivation of the mass of an electron, and in fact in all problems of a similar nature, many will doubtless object to this assumption on the ground that probably the ordinary electrical laws do not apply when the distance between "elements of charge," so called, is comparable with the diameter of an electron.

Although it is difficult to see how a coherent mathematical theory of electricity can at present be formed without this assumption, yet it was thought best to add a more general proof of (17). The following is therefore given as avoiding the explicit use of constraints.

17. The statement of the law of the conservation of energy for an element of volume in any electrical system possessing electrical charges in motion, is the well-known expression

$$\frac{\partial w}{\partial t} = -\left(\frac{\partial \mathbf{S}_x}{\partial x} + \frac{\partial \mathbf{S}_y}{\partial y} + \frac{\partial \mathbf{S}_z}{\partial z}\right) - (v_x \rho \mathcal{F}_x + v_y^* \rho \mathcal{F}_y + v_z \rho \mathcal{F}_z) . \tag{23}$$

Here (w) is the density of the total electromagnetic energy,  $S_x$ ,  $S_y$ ,  $S_z$  are the components of the Poynting vector,  $\mathscr{F}_z$ ,  $\mathscr{F}_y$ ,  $\mathscr{F}_z$  are the components of the total electromagnetic force on unit charge,  $(\rho)$  is the density of electrification at the given point, and  $v_x$ ,  $v_y$ ,  $v_z$  represent the velocity through space of this electrification. Thus

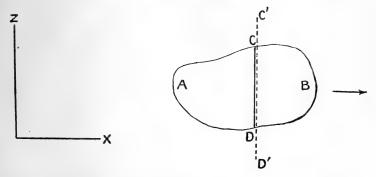
$$w = \frac{1}{8\pi} \{ (X^2 + Y^2 + Z^2) + (\alpha^2 + \beta^2 + \gamma^2) \},$$

where X, Y, Z, and  $\alpha$ ,  $\beta$ ,  $\gamma$ , are the electric and magnetic force intensities respectively, and

$$\begin{aligned} &\mathscr{S}_x = \mathbf{X} + (v_y \gamma - v_z \beta), \\ &\mathscr{S}_y = \mathbf{Y} + (v_z \alpha - v_x \gamma), \\ &\mathscr{S}_z = \mathbf{Z} + (v_x \beta - v_y \alpha). \end{aligned}$$

Equation (23) states merely that the rate of increase of energy in an elementary volume is equal to the activity of any foreign (i.e., non-electrical) forces which may act therein minus the outward flow of energy.

Now suppose we consider an electromagnetic system bounded by a rigid surface (AB), which moves uniformly



through space with the velocity  $(v_1)$  along the axis of (x); and further suppose that the volume inside this closed surface is divided into two parts by the plane partition (CD) which is perpendicular to the x-axis and which, although fixed in the moving system, coincides at a given instant with the plane (C'D') fixed in space. If this system be considered as isolated, then no disturbance passes through the bounding surface (AB).

In equation (23) the time derivative of the energy density *Phil. Mag.* S. 6. Vol. 15. No. 85. *Jan.* 1908.

refers to a point fixed in space, and if we wish it to refer to a point moving with the system we must write as usual

$$\frac{\partial w}{\partial t} = \frac{\partial' w}{\partial t} - v_1 \frac{\partial w}{\partial x}, \qquad (24)$$

where  $\frac{\partial^2 w}{\partial t}$  now means the rate of change measured from the

moving point. Likewise, if we wish the velocities which enter into (23) to be expressed in terms of velocities relative to axes moving with the system, we must write

$$\begin{cases}
v_{x} = v_{1} + v_{2x} \\
v_{y} = v_{2y} \\
v_{z} = v_{2z}
\end{cases}$$
(25)

where  $v_{2x}$ ,  $v_{2y}$ , and  $v_{2z}$  are the components of these relative velocities.

Substituting (24) and (25) in (23), and remembering the simple proportionality between  $S_x$ ,  $S_y$ , and  $S_z$  and the density of momentum  $m_x$ ,  $m_y$ , and  $m_z$ , we easily obtain

$$V^{2} \frac{\partial m_{x}}{\partial x} - v_{1} \frac{\partial w}{\partial x} + v_{1} \rho \mathscr{F}_{x} = -\frac{\partial' w}{\partial t} - \left(\frac{\partial S_{y}}{\partial y} + \frac{\partial S_{z}}{\partial z}\right) - \left(v_{2x} \rho \mathscr{F}_{x} + v_{2y} \rho \mathscr{F}_{y} + v_{2z} \rho \mathscr{F}_{z}\right). \qquad (26)$$

Now  $(\rho \mathscr{S}_x)$  may be expressed in terms of the electric and magnetic force intensities, together with the density of the momentum. This involves only the fundamental equations of electromagnetic theory and has been done in paragraph 7, reference to which will show that with the present notation

Substituting this for the  $(\rho \mathscr{F}_x)$  which occurs on the left-hand side of (26), rearranging the latter, and putting

$$w = rac{1}{8\pi} \{ X^2 + Y^2 + Z^2 + lpha^2 + eta^2 + \gamma^2 \}$$
 and  $w_t = rac{1}{8\pi} \{ Y^2 + Z^2 + eta^2 + \gamma^2 \},$ 

$$\frac{\partial}{\partial x} \left\{ (\nabla^2 + v_1^2) m_x - 2v_1 w_t \right\} 
= -\frac{\partial' w}{\partial t} + v_1 \frac{\partial' m_x}{\partial t} - \left( \frac{\partial S_y}{\partial y} + \frac{\partial S_z}{\partial z} \right) 
- \frac{\partial}{\partial y} \left\{ \frac{1}{4\pi} (XY + \alpha\beta) \right\} - \frac{\partial}{\partial z} \left\{ \frac{1}{4\pi} (XZ + \alpha\gamma) \right\} 
- (v_{2x}\rho \mathscr{F}_x + v_{2y}\rho \mathscr{F}_y + v_{2z}\rho \mathscr{F}_z) \dots (28)$$

Now if this expression is integrated through the part of the volume (AB) which lies on the side (A) of the partition (CD), the terms on the left of (28) become equal to

$$\int \{ (\nabla^2 + v_1^2) m_x - 2v_1 w_t \} dS,$$

where the integral is taken over the part of the plane (C'D') which is included in the surface. This follows from the fact that the rest of the surface of part A belongs to the surface (AB) and outside of (AB) there is no disturbance whatever. The terms on the right (of 28) give an average value of zero. This last will be evident if they are considered separately. The first two give directly a time average of zero, after great elapse of time, since neither (w) nor  $(v_1m_x)$  ever becomes infinite. The terms involving the (y) and (z) derivatives when integrated may be written as surface integrals over the bounding surface (of part A), and they then represent the flux of energy through this surface in a direction perpendicular to  $(v_1)$ , i. e., in a direction perpendicular to the x-axis. This flux being everywhere zero over the surface, these terms vanish.

The terms involving  $\mathscr{F}_x$ ,  $\mathscr{F}_y$ ,  $\mathscr{F}_z$  also give a time average of zero because they represent what might be called the "internal activity" of the forces which act on the charges in the Apart of the volume (AB), and since this part A is isolated on all sides except on the side (CD), the activity of these forces really means the rate at which the part (B) by means of them is doing work on A. In the long run B's work on A must be equal to A's work on B, if the system is to be conservative and the internal motions are to be stationary.

Thus we learn finally from equation (28) that the average value of

$$\int \{ (\mathbf{V}^2 + v_1^2) m_x - 2v_1 w_t \} d\mathbf{S} = 0,$$

where the integral is taken over the enclosed part of the plane (CD). Since this is true for any position of the plane (CD) so long as it is perpendicular to  $(v_1)$  we evidently have on

the average, integrating along (x) throughout the entire system,

$$\int \{ (\nabla^2 + v_1^2) m_x - 2v_1 w_t \} d\tau = 0. \quad . \quad . \quad (29)$$

This gives, using the former notation, and remembering that on the average the internal structure is assumed to remain the same,

$$M_x = \frac{2v_1 W_T}{V^2 + v_1^2} = \frac{2v_1 W_T}{V^2 \left(1 + \frac{{v_1}^2}{V^2}\right)} \quad . \tag{30}$$

which, since  $(v_1)$  is here along (x), is precisely the result of equation (16), and becomes (17) on differentiation.

#### Conclusion.

It has been shown in the foregoing that the electromagnetic mass of an isolated, symmetrical, purely electric system possessing any structure which on the average remains the same, and any internal motions or constraints, is expressible in terms of its velocity as a whole through space together with its "transverse energy" and the derivative of the latter with respect to the velocity. If second-order terms in the velocity be neglected, the mass is a simple constant multiplied by the total included electromagnetic energy.

If the mass of ponderable bodies has an electromagnetic origin, then the inertia of matter is to be considered merely as a manifestation of confined energy. From this point of view, matter and energy are thus very closely related and the laws of the conservation of mass and energy become practically

identical.

It has been pointed out that the loss of mass, inevitable on this view, which takes place when energy is lost to the system, is large enough to be detected in the case of radioactive changes. If we assume the disintegration theory of the elements, this loss of mass affords a ready explanation of the general, small irregularities to be found in the list of atomic weights, and thus removes a serious difficulty from the path of the disintegration theory. For this loss of mass to take place however, it is not necessary that the whole of the mass be electromagnetic.

It has been shown that if material mass be electromagnetic and if lighter elements are formed from heavier ones through violent energy changes, it follows that gravity acts between quantities of confined energy and not between masses in any other sense. Several speculations are indulged in as to the results of assuming gravitation between quantities of energy.

Finally, the fundamental proposition is dealt with mathematically from an entirely different point of view and the same result obtained.

In conclusion I wish to express my thanks to Prof. J. J. Thomson and to Mr. G. F. C. Searle for several valuable criticisms and suggestions.

Cambridge, England, August 14th, 1907.

## II. The Evolution and Devolution of the Elements. By A. C. and A. E. Jessup \*.

### [Plate VII.]

THE hypothesis that the elements are different forms of one original substance was first formulated in modern times by Prout, and though his idea that hydrogen was that substance has since been shown to be incorrect, yet modern theories have given us, in the corpuscle, a body which may well be the root basis of all matter.

The recent researches of M. and Mme. Curie, Sir William Ramsay and Mr. Soddy, Professor Rutherford and others, have brought to light the fact that some of the elements are undoubtedly degrading into simpler forms of matter. But when we look for a reversal of this process on the earth, it is not apparent. In other words, we have as yet found no indications that elements with low atomic weight are changing into other elements with a higher atomic weight, that is, we have no proof of inorganic evolution. But when we turn our attention to the heavens, the case is altered, and it is entirely upon astrophysical observations that the ideas of evolution we are about to bring forward are based.

It was originally our intention to give these observations in full, but it has appeared advisable to give in the present paper only such of them as are essential for an understanding of what follows.

Spectroscopic evidence shows us that the nebulæ contain but few elements, all of which are in a highly attenuated form. The only two which have been recognized on the earth are hydrogen and helium, and the atomic weights of these are less than those of any other elements with which we are acquainted.

As the nebula becomes more compact, and assumes the form of a star, more and more complex elements appear, such

<sup>\*</sup> Communicated by Sir William Ramsay, K.C.B., F.R.S.

as iron, carbon, calcium, silicon, and magnesium, whose presence is first evidenced by their enhanced lines, as shown by Sir Norman Lockyer. The enhanced lines of the elements are known to be due to the elements being submitted to very high temperatures or very great electric stresses. Inasmuch as we are justified in assuming the existence of stresses in the stellar systems, it is justifiable to assume the existence of enhanced lines as first evidences of evolution. Moreover, it may be pointed out that the appearance of new lines in the nebulæ is generally accompanied by a faint continuous spectrum, usually in the green. Hence, in the heavens, it would seem that we have distinct evidence of evolution.

Now Mendeléeff has arranged the elements in order of atomic weight, and in such a way that they fall into groups, and we may regard the evolution as taking place in one of two ways. Firstly, that the elements evolve in order of atomic weight, that is along horizontal lines of Mendeléeff's table; secondly, that they evolve in groups, that is, down its vertical columns. We have strong reasons for believing that

the second method has most evidence in its favour.

In the first place, the elements which appear after hydrogen and helium are carbon, silicon, magnesium, calcium, and iron, but these are in no way in order of their atomic weights, and moreover sodium, although much smaller quantities of it can be detected, and with a much lower atomic weight than calcium or iron, does not appear until long after these elements. The first positive evidence of sodium is in the case of the stars of group 7.

Secondly, the whole of the nitrogen group is missing in the sun. On the supposition that the elements grow in groups, the fact that nitrogen did not form in the sun would account for the absence of the other members of its family. The other method of growth would imply, that each of the five elements belonging to the group was missed out in the

ordinary process.

Our view of evolution will at once explain two great difficulties connected with the Periodic Table, namely, the cases of tellurium and argon, with atomic weights greater than those of iodine and potassium. It is natural to assume, that if an element A has a greater atomic weight than an element B, the element formed from A will also have a greater atomic weight than that formed from B; but this is not necessary, and the two cases cited above are examples of this fact. Sodium, with a greater atomic weight than neon, forms potassium, which has a less atomic weight than argon.

However, to return to the first stage of evolution. The

nebulous stage of matter is the first of which we have any The spectra of the very earliest nebulæ consist of three lines only, their wave-lengths being 5007, 4959, and 4862 t.m., and corresponding to hydrogen and two unknown As a nebula grows more compact, two more lines appear with wave-lengths 4340 and 5876 t.m. These are due to hydrogen and helium respectively. Consequently, we might well suppose that in the nebulous stage of matter there are four substances, the first two being unknown upon earth, the third being hydrogen, and the fourth, which apparently only exists in small quantities, being helium. It also seems probable that except these four, no other elements exist in the early nebulæ; and if this is the case, we are justified in assuming that hydrogen, the two unknown elements, and helium are the four original elements from which all the other elements form. To distinguish them from the others we will term them protons.

Before specifying which elements these four protons produce, it will be as well to indicate as briefly as possible the manner by which we consider that one element gives rise to

another.

We may assume that all matter at some period was in the form of corpuscles. By certain processes, a description of which we hope to give in a future paper, some of these corpuscles arranged themselves into stable integral systems, these systems being the four protons. These protons in turn developed into other atoms. Each of these protons begins to collect round it more corpuscles, this condensation continuing until a stable system is formed, capable of separate existence.

The assemblage round the central atom may be regarded as having certain properties, and a more or less definite shape. We do not propose to speculate at all on the nature of this assemblage, beyond saying that the particles are probably in rapid motion, and that the whole atom forms a stable system. We may, however, for convenience denote this assemblage by the term "ring." If the atoms were really built up of concentric rings, all that we have to say would apply equally well, so that in order to imagine the appearance of an atom, we may actually look upon it as composed of a series of rings of varying shape and size, and in all that follows we shall speak as though this were its actual structure, for the sake of simplicity; but it must be distinctly understood that we make no assumption as to its true form. We may here mention that the formation of successive elements is attended by the escape of a large quantity of energy, and that the systems are steadily progressing from a higher to a lower energy content.

fact, we may go so far as to say that the whole process of evolution is entirely governed by the possibility of energy

leaving the systems.

The process of evolution may be considered to be a perfectly smooth and continuous one, and the elements as we know them only to represent positions of maximum stability, which are arrived at during the process of evolution. Since the elements may be looked upon as denoting the positions of maximum stability or, so to speak, stopping places in the evolution process, we can readily comprehend the simultaneous existence of all the elements. Of course the rate of evolution along different groups may vary, and therefore we are not surprised at the fact that calcium and iron, with atomic weights of 40 and 56 respectively, are found in stars which do not contain sodium with an atomic weight of 23.

We will now turn our attention to the periodic table as given by Mendeléeff and see how far our ideas of evolution agree with the form of the table as given by him. Several attempts have been made to remodel this table, of which perhaps the most notable are the harmonic periods of Professor Emerson Reynolds, the vibrating pendulum of Sir William Crookes, and the logarithmic spiral of Dr. Johnstone Stoney. It is, however, admitted that there are defects in all of these, and we hope to be able to remove some of them. We may perhaps here mention that the idea of evolution in groups was first suggested by Mendeléeff's table, and that without it our original observations would not have developed. It was only when we came to extend our ideas that we found that they would not entirely agree with the table as it originally stood. Consequently, we have in our turn ventured to present the table in a modified form, which we hope may smooth over some of the difficulties at present connected with the classical researches of the great Russian.

In the table as it now stands, it is customary to divide the main groups into two sub-groups. For instance, group I is in Mendeléeff's table divided into group I A. hydrogen, lithium, sodium, potassium, rubidium, and cæsium; and

group I B. copper, silver, and gold.

Now, it will at once be seen that although all the elements of the same sub-group resemble each other greatly, yet members of different sub-groups have apparently very little connexion between them. Members of the same sub-group occupy corresponding positions on the atomic volume and melting-point curves, while the positions of members of different sub-groups differ very widely.

The same considerations apply to group II. if it be subdivided as follows:—A. Beryllium, magnesium, calcium, strontium, barium, radium; and B. zinc, cadmium, mercury. However, in chemical properties there is a certain relationship

between the two sub-groups.

In group III., though the members of the different subgroups occupy different positions on the two curves mentioned above, yet their chemical properties are more closely connected than those of group II. If we proceed in this manner through the groups, we shall in all cases find the members of corresponding sub-groups differing with regard to their positions on the curves, and varying the closeness of their chemical relations as they pass from group to group. In groups 3, 4, and 5 the members are most alike, while those in groups 1 and 7 are most dissimilar.

To account for these facts we venture to put forward the following explanation. We would suggest that members of each sub-group evolve in turn from the first member of that group, and resemble each other in structure. All the members of a single Mendeléeff group do not evolve from each other in order of atomic weight, but only each sub-group, the two sub-groups of each column have an entirely different internal atomic structure, their apparent resemblance being wholly due to a similarity in the external form of their atoms. This question will be more fully discussed later, but at present we must investigate the result this assumption will

have on the form of the periodic table.

In the first place, it is evident that if each sub-group be considered as being the result of a separate and distinct process of evolution, an increase in the number of sub-groups must be made. To determine what the number shall be, it is best to consult the atomic volume curve. It is generally admitted that lithium, sodium, potassium, and rubidium are typical members of one family, as is clearly shown by their positions on the above-mentioned curve. Between lithium and sodium are seven elements, and the same number is found between sodium and potassium, but between potassium and rubidium there are seventeen. This means that in the horizontal series, starting with lithium and sodium, there are eight groups, but in the next series this number has increased. An explanation of this is that one or more of the elements in the second series of eight has developed in more than one way.

Lest this seem improbable, we may mention that it is exceedingly unlikely that there are more than four original elements or protons, while it is universally acknowledged that the series starting with lithium and sodium both contain

eight members. Consequently, if our idea of evolution is to hold good, one at least of these protons must have given rise

to more than one direct product of evolution.

If it be admitted that some double growth has occurred, the next step is to find the place of its occurrence. Examining the atomic volume curve, we find that sodium and potassium, magnesium and calcium occupy similar positions on the curve, and also that the same relations hold good between phosphorus and arsenic, sulphur and selenium, chlorine and bromine: and, consequently, these pairs must be directly connected together in the process of evolution. Now sodium and potassium, magnesium and calcium, are corresponding members of consecutive horizontal series of Mendeléeff's table; but the three next pairs, phosphorus and arsenic, sulphur and selenium, chlorine and bromine, do not belong to two consecutive horizontal series, for the elements vanadium, chromium, and manganese, respectively, lie between the members of these pairs. We may conclude, therefore, that the evolution must have sub-divided at some position between magnesium and phosphorus; in other words, that either aluminium or silicon, or both, must have given rise to more than one series of evolution products.

Now potassium and sodium, calcium and magnesium, arsenic and phosphorus, selenium and sulphur, bromine and chlorine must be consecutive products of evolution in their respective families, and we are driven to the conclusion that vanadium cannot be derived from phosphorus at all. Similar arguments apply to chromium, manganese, &c. We are therefore justified in concluding that vanadium, chromium, manganese, &c., must be derived by indirect evolution from

aluminium or silicon.

If we compare the chemical characteristic properties of boron, aluminium, and scandium, with those of lithium, sodium, and potassium, and of beryllium, magnesium, and calcium, the analogy between the three groups is sufficiently strong to justify our considering scandium as the direct derivative of aluminium, and, for the same reasons, we must consider titanium to be the direct derivative of silicon. Now, silicon and phosphorus undoubtedly follow one another in order of atomic weight, i. e., there are no elements of atomic weight lying between 28·4 and 31·0; and inasmuch as titanium and arsenic have been shown to be direct evolution products of silicon and phosphorus, it is quite evident that all the elements possessing atomic weights lying between that of titanium (48·1) and arsenic (75) must be derived from silicon by indirect processes of evolution.



H.	1.01	p.Be.	1.33	p.B.	2.						
Li.	7.03	Be.	9.1	В.	11	C.	12.				
Na.	23.05	Mg.	24:36	Al.	27.1	Si.	28.4				
к.	39.15	Ca.	40.1	Sc.	44.1	Ti.	48.1	V.	51.2	Cr.	CT
Rb.	85.5	Sr.	87.6	Y.	89.0	Zr.	90.6	Nb.	94.0	Mo.	. 6
Cs.	132.9	Ba.	137:4	La.	138.9	Ce.	140.3				
		Tm. ?	171	<b>Y</b> b. 3	173			Ta.	183	w.	18
		Ra.	225			Th.	232.5			σ.	23

There are now ten elements lying between these limits, viz., vanadium, chromium, manganese, iron, nickel, cobalt, copper, zinc, gallium, and germanium; and we must consider all these to be derived from silicon by some indirect process of evolution. It may be pointed out here that by the term "A direct process of evolution," we mean one by which an evolution product is obtained of the same valency as its parent or immediate antecedent element in the scale of evolution. Conversely, "indirect evolution" produces elements of

valencies differing from that of the parent element.

Now the next highest elements to germanium in order of atomic weight are arsenic, selenium, bromine, krypton, rubidium, and strontium; but these undoubtedly belong to the families of nitrogen, oxygen, fluorine, helium, lithium, and beryllium respectively, and so may be considered as the direct evolution products of these families. The next four elements again are yttrium, zirconium, niobium, and molybdenum, and these will fall naturally under scandium, titanium, vanadium, and chromium respectively, a fact which is in absolute agreement with the relative chemical properties of the families concerned.

We are now in a position to draw up a Periodic Table modified from that of Mendeleéff so far as to embody our

conclusions, and such a table is shown opposite.

Leaving, for the moment, the question of the four protons, hydrogen, proto-beryllium, proto-boron, and helium, we have clearly eight elements standing at the head of eight very strongly characterised families, viz., lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine, and neon. By direct evolution these eight elements give rise to the next eight elements in order of atomic weight-sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, and argon. The question of argon having an atomic weight greater than that of potassium has already been mentioned. Following on, we have potassium, calcium, scandium, and titanium, which belong to the first four groups of the table. After titanium, we have the ten indirect derivatives of silicon which we have dealt with above, and we therefore place these in a horizontal row between the carbon and the nitrogen families. The next ten elements in order of ascending atomic weight following germanium, viz., arsenic, selenium, bromine, krypton, rubidium, strontium, yttrium, zirconium, niobium, and molybdenum, fall perfectly naturally in the consecutive families as already pointed out. The next vertical column after molybdenum is headed by manganese; from a consideration of Mendeléeff's table, it is quite evident that

## THE PERIODIC TABLE.

H.	1.0	)1 p.B	le. 1	33 p.	.В.	2.												_																-	He.	4
Li.	7.0	Вe.	9.	1 B	3. 1	11	C.	12.							-														N.	14.01	0.	16.0	F.	19	Ne.	20
Na.	23.0	)5 Mg	. 24	36 <b>A</b>	d. £	27-1	Si.	28.4						_		•								~				_	P.	31.0	S.	32.00	C1.	35.45	Ar.	39.9
K.	39.	5 Ca.	10.	l S	с	14-1	Ti.	48:1	v.	51:	Cr.	52·1	Mn.	55·0 <b>F</b> 0	e.	55.9	Ni.	,59.	7 Co.	59.(	Cu.	63.6	Zn.	62.4	Ga.	70	Ge.	72.5	As.	75.0	Se.	79.2	Br.	80.0	Kr.	81.8
Rb.	85-8	Sr.	87	G Y	r. 8	39-0	Zr.	90•0	Nb.	94.	Mo.	96-0	1	R	u. :	103.0	Rh.	103	Pd.	106:3	Ag.	107.9	Cd.	112.4	In,	115	Sn.	119.0	Sb.	120.2	Te.	127.6	<b>I</b> .	127.0	Xe.	128
Ca.	1324	Ba.	. 137	4 L	a. 1:	3s-9	Ce.	140:3	3					P	r. ?	140 5	Nd.?	143	Sm.	? 150·3	Eu. ?	151.7		ŀ	Gd.?	157			Tr. ?	160	Er.	166				
		rm	. ? 171	Y	7b. ? 1	7:3			Ta.	183	w.	184		05			Ir.	193	Pt.	194.8	Au.	197-2	Hg.	200-0	Tb.	204.1	Pb.	206.9	Bi.	208.5						
		Ra	, 225				Th.:	232-5			<b>ٿ.</b>	238-5							[													-	-			



manganese has no direct evolution products, that is to say, there are no elements of higher atomic weight than manganese with properties sufficiently closely related to manganese to justify our considering them as direct evolution products of this element. We have therefore placed manganese at the head of its own column, and would point out that the blank spaces below this element do not necessarily mean that there is room for elements to be discovered to fill these, for, as will be presently shown (page 36), it is in the highest degree improbable that manganese should be able to give rise to any direct derivatives at all.

Following molybdenum, we have now the three elements ruthenium, rhodium, palladium, which clearly may be placed under iron, nickel, cobalt. After these three come in ascending order twelve elements, silver to cerium, which fall naturally into consecutive families as shown in our table. Between cerium and tantalum we have all the rare earths, and indeed, so little is known of their chemical properties that it is impossible to assign any of these to its particular family with any degree of confidence. We have, however, ventured to assign positions to those rare earths which seem to be known definitely, and have followed Emerson Reynolds' example in considering praseodymium, neodymium, and samarium as belonging to the iron group. We are convinced that the rare earths are very abnormal: they are all characterized by being trivalent, and this fact alone, which means that the external atomic structure is that of a trivalent element, is sufficient to differentiate these from the other normally developed elements, for in most cases they cannot be evolved simply from trivalent antecedents. However, in the section of this paper which deals with the question of radioactivity, we put forward a suggestion which may account for their extraordinary characteristics. The remaining elements after tantalum up to uranium may, without question, be assigned to the positions shown in our table.

We may now turn our attention to the four protons, that is to say, the four earliest forms of matter existing in nebulæ, viz., those with wave-lengths 4862, 4959, 5007, and 5876 t.m., and endeavour to trace how the process of evolution from these gave rise to the eight elements lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine, and neon. We feel that we are justified, in dealing with processes of evolution, in saying that the most natural tendency will be for the process to take place along a direct line of development. It is reasonable to assume that the probable effort of any element will be to give rise to an element of its own type. We would

urge that in elementary evolution, the principle of heredity is an all-important one, and that the normally derived elements would be characterized by the same properties as the antecedent elements in each case. Now, in the case of the lightest proton, hydrogen, its chemical behavour is that of a monovalent element; and from our standpoint of the existence of the principle of heredity (see page 51), we consider that the direct descendants of hydrogen must be monovalent elements, or, in other words, that hydrogen must be the antecedent element of the alkali metals, and therefore we have placed hydrogen at the head of this family \*. An exactly similar argument is applicable to the fourth proton helium, and we therefore place helium in the last group of our Table, thereby establishing it as the progenitor of the inactive

gases.

We now have left two protons, viz., those with wavelength 4959 and 5007 respectively. Clearly these two must in some way have given rise to all the elements except the alkali metals and the monovalent gases. In our table, we have placed the proton with wave-length 4959 at the head of the alkaline earth metals and the remaining proton at the head of the trivalent third group. Now inasmuch as we know at present nothing of the chemical properties of these two unknown elements, it is clearly impossible for us to make any definite statement as to how the evolution proceeded from them. Our reasons, however, for placing these two elements in the positions assigned to them are as follows: -(1) Hydrogen has an atomic weight of one, helium of four. The wave-length of the hydrogen line is 4862, and that of the helium line is 5876. We therefore assume that the element whose wave-length is 4959 has a smaller atomic weight than the element with wave-length 5007. (2) Silicon gives rise to a great number of elements, many of which are to be found in considerable quantities, both in the earth and in the stars. It is only reasonable therefore to conclude from this that the original proton from

<sup>\*</sup> At first sight, it might be pointed out that hydrogen can be considered as the progenitor of the halogen family, inasmuch as these elements are usually spoken of as being monovalent. Against this, however, we point out that the monovalency of the alkali metals is equal and opposite to that of the halogens. The former are monovalent in the fact that they have one free electron to be given up when entering into combination, while the latter are monovalent in the fact that they take up one electron in forming compounds. Hydrogen and the alkali metals are absolutely analogous in their compounds with the halogens. If hydrogen belonged to the halogen group, hydrogen should be more electronegative than fluorine, and should form mono-atomic compounds with the alkali metals, more stable than the fluorides.

which silicon was evolved should be found in very large quantities in the nebulæ. Now the element whose wave-length is 5007 is far the most abundant of the four protons formed in the nebulæ, and consequently, we consider that this element gives rise to carbon and silicon, &c. (3) Starting from lithium, in the whole scheme of evolution there is only one point where the evolution sub-divides into both direct and indirect series of derivatives. This occurs, as we have shown, in the case of the element silicon, which gives rise to one direct and ten indirect derivatives, and applying our hereditary principle, we would say that this tendency to sub-divide is due to the fact that such a sub-division had previously taken place, and would therefore argue that carbon and silicon are themselves indirect derivatives from one of the protons. For this reason, therefore, we think that the position of the element 5007 cannot be at the head of the carbon and silicon groups. (4) Moreover, except in the case of the six central groups, the discussion of which, owing to their exceptional character. we for the moment defer, there is no case in the whole table of an element giving an evolution product with a valency less than its own \*. For these reasons we put the proton with wave-length 5007 at the head of the trivalent groups of elements boron, aluminium, &c., and we are only left with the position at the head of the alkaline earth metals for the remaining proton with wave-length 4959. Since this element has without doubt a smaller atomic weight than that of the element with wave-length 5007, this position seems perfectly For convenience we venture to suggest the names of proto-beryllium and proto-boron for these two elements.

Since drawing up this Periodic Table, a paper has appeared by Messrs. Cuthbertson and Metcalfe (Phil. Trans. 1907, Ser. A, vol. cevii. p. 135), in which they give a Periodic Table of the Elements, which, so far as it is carried, is practically the same as the one in this paper. These authors have deduced their Table from observations upon the refractivities of the elements, and we venture to think that this gives considerable support to this particular form of the Periodic Table.

In our new form of the Periodic Table it will be observed, as already pointed out, that a large number of elements appear as having been formed from silicon. Now, to explain their position, and in fact, the actual structure of all the

<sup>\*</sup> By our theory of the indirect evolution process, the indirect products must have a greater valency than the parent element (see below p. 33).

atoms, it will be necessary to enter more fully into the

question of rings, to which we have already alluded.

As was stated in our preliminary description of the process of evolution, we consider that originally all matter was in the form of corpuscles, and that some of these corpuscles arranged themselves into stable integral systems, these systems being the four elements: hydrogen, proto-beryllium, proto-boron, and Each of these elements began to collect round it more corpuscles, and this continued until another stable system was formed, capable of separate existence. system or assemblage of corpuscles around the central atom may be regarded as having certain properties, and a more or less definite shape. We denoted this assemblage by the term "ring," it being understood that we make no assumption as to its true form. We, however, consider each ring to have a definite structure, and certain properties depending on that structure: in fact we conclude that all the principal chemical properties of each element are entirely determined by the structure of the ring.

Now each ring may be supposed to consist of two parts: (a) the main assemblage of corpuscles, to which the ring owes its mass, size, and shape, and (b) a certain number of corpuscles which are attached to the rest in a slightly different manner. They may be perhaps regarded as satellites to the main ring, although their connexion is probably much closer than that suggested by this illustration. For the sake of distinction from the other corpuscles we will apply the term

"electron" to them.

From a general study of these electrons there is undoubtedly a tendency possessed by them to form into systems of eight, or multiples of eight, during the process of evolution. These sets of electrons constitute, in some way or another, electrically neutral systems. For example, we feel convinced that all phenomena of chemical combination are due to this tendency. Thus, if an atom with two electrons is brought into immediate contact with one possessing six, the two electrons will leave the first atom, and form a very stable system of eight electrons around a second atom; and, as we say, upon this fact depends the combining power and the valency of each element. A fuller discussion of this may well be deferred until we have entered into the process of evolution in greater detail.

It will be advantageous in doing this to take a specific instance, and for this purpose we will take the element hydrogen. As our Table shows, we consider that hydrogen is the progenitor of all the alkali metals. Now the hydrogen atom is a

monovalent element, that is to say the outer ring of corpuscles belonging to hydrogen contains one free electron, the whole constituting a stable system. We have already stated that the tendency of the electron is to form into stable groups of eight, consequently we may view the single free electrons of hydrogen as being possessed with a definite and measurable desire to complete its system of eight. It appears that in order to do this it adds on first a single group of eight electrons. The result of this would be that the free electron on the hydrogen atom completes its system of eight, and that one electron will still be left over in the free state. This addition of systems of eight electrons goes on continuously until the next position of maximum stability is reached. This, however, as we have before shown, represents the element lithium. Now inasmuch as the addition of each group of eight electrons in adding itself on, forms with the free electrons already existing a stable group of eight, and leaves still one free electron on the outside, so now we see that each evolution product thus normally produced must have the same valency as the antecedent element. We therefore find that lithium and all the elements normally produced from hydrogen must be monovalent. Now without binding ourselves down in any way to the actual shape of these rings, we do assume that there is some intimate connexion between the valency of a ring and its shape. We therefore point out that in the process of evolution from hydrogen each ring and corpuscle takes on the same shape as the outer ring of the hydrogen atom; that is to say, that the rings of all the alkali metals have that shape which is typical of the ring of the hydrogen Now this addition of rings of the same type as the previously existing rings is what we have already spoken of as the principle of heredity, that is to say, in all normal processes of evolution there is definite evidence of an hereditary principle, inasmuch as every valent element possesses the same shape and valency as that of its antecedent element. Now this process of evolution, which we have described in detail in the case of the alkali metals, we consider to be perfectly general throughout the whole of the Periodic Table, in so far as what we have called "direct evolution" is concerned. This normal process of evolution takes place undoubtedly in the first three families, and in the last family of our Table.

The next point we have to deal with, is what we have previously defined as "indirect evolution"; that is to say, when series of elements of valency differing from that of the parent family are produced. In the case of the first group of alkali metals, the members of this family are amongst the most electro-positive of all the known elements; that is to say, they possess a very great tendency to enter into combination. In the second group, which possesses two free electrons and contains the metals of the alkaline earths, this tendency is great, but considerably less than in the group just mentioned. In the third group this tendency is still further reduced, with the result that the tendency of the three electrons on the outer ring of these elements to complete themselves into systems of eight is very materially smaller than in the case of the first two groups of the Table. Consequently, although we have a normally evolved series of elements from protoboron, we also have an indirectly evolved element in carbon. We venture to suggest that this may be explained as follows:—

The element proto-boron in its normal process of development, produces the element boron. It, however, is capable of proceeding along the lines of indirect evolution also, and thus gives rise to the element carbon. Instead of proceeding directly along the normal lines from boron to aluminium it does not add on complete rings of electrons, but only takes up an insufficient number of sets of eight electrons. These sets of eight electrons are absorbed into the outer ring, with the result that a new outer ring is formed of different shape, viz., a tetravalent ring. The three electrons in the outer ring of boron are not sufficiently desirous of forming complete systems of eight to compel the evolution to proceed as far as aluminium, but they will allow the incorporation of a small number of sets of eight electrons, with the result that instead of abstracting five electrons to complete their own system they only abstract four, so that the outer ring of the new element becomes tetravalent. The acceptance of a smaller number of the sets of eight electrons than is necessary to produce a complete ring is possible by the incorporation of these sets in the previously existing ring, so that a new ring of an altered type is produced. This new type of ring we define as a "distorted" ring, and we may go so far as to say it has a greater valency than the original ring. would point out that when the process of indirect evolution takes place, and the so-called distorted ring is produced, the first step is the establishment of the new ring which then proceeds to develop normally until the first position of maximum stability is reached. Thus, in the indirect evolution from proto-boron, the first stage is the incorporation of the necessary sets of eight corpuscles with the establishment of the tetravalent ring belonging to the first family of indirect derivatives (carbon, silicon, &c.). This tetravalent ring then

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can evolve normally until the first position of maximum stability is reached—carbon. It follows from this, therefore, that the formation of these distorted rings (or in other words "indirect evolution") only first becomes possible with trivalent elements, and that it is very likely to take place with tetravalent elements. We press this conclusion on the argument previously developed, that a tetravalent element will be still less desirous of completing the system of eight electrons than even a trivalent element. As a natural sequence of this, we should expect to find that the element silicon would show an exceptional tendency towards this phenomenon of indirect evolution, and, as a matter of fact, as we have already shown, the element silicon gives rise to a great number of indirect derivatives. It is important to notice that neither of the elements proto-boron or silicon gives only one series of indirect derivatives, for in the former case we have in addition to carbon the elements nitrogen, oxygen, and fluorine; and in the latter case we have vanadium, chromium, and manganese. We are convinced that there is some fundamental reason underlying the production in this way of several indirect derivatives. Taking the case of the indirect evolution from the element proto-boron, it will be seen that we have derived in this way the elements carbon, nitrogen, oxygen, and fluorine; that is to say, a tetravalent, a pentavalent, a hexavalent, and a heptavalent element.

In speaking of the valency of an element we define this as the number of electrons which that element gives up in entering into combination: thus lithium is monovalent, beryllium is divalent; nitrogen is pentavalent, because it gives up five electrons; so that we speak of nitrogen, oxygen, and fluorine as being penta-, hexa-, and hepta-valent

respectively.

Now we have already shown that in the case of the element carbon, the formation of this element is caused by the absorption of a number of the sets of eight electrons which in themselves are insufficient to form a complete ring. The result is that the distorted tetravalent ring which gives rise to carbon is formed; and furthermore, the three free electrons on the outer ring of the antecedent element have not taken up five electrons to form a set of eight, but only four. In the case of the element nitrogen an almost identical procedure takes place, only in this case three electrons have been extracted in place of the normal five, with the result that a second type of distorted ring is produced with a valency of five.

In the case of the element oxygen a similar absorption of

sets of eight electrons takes place, but only two electrons are taken up by the outer ring of the antecedent element, with the result that a distorted ring is produced of valency six.

In the case of the element fluorine we have a distorted ring of valency seven produced in exactly analogous fashion. We would point out that from this point of view a trivalent element can only give rise to four indirect derivatives, and all of these possible derivatives are accounted for in our Table.

The next case we have to consider is that of the element silicon. This is a tetravalent element, and consequently can only give rise to three indirect derivatives, viz., a pentavalent, a hexavalent, and a heptavalent element. Thus from silicon we have the direct derivative titanium, this being the case when the superadded ring gives up four electrons to complete the system with the four already existing electrons on the four-membered ring of silicon.

We then have the first indirect derivative in which a distorted ring is produced of valency 5, when only three electrons are transferred. This is the case with the element vanadium. We have the third and fourth indirect derivatives chromium and manganese which possess distorted rings of

six and seven valencies respectively.

Now each of those elements which has been produced by a process of indirect evolution such as we have described, may itself become the source of new elements and families of elements produced from it by normal or direct processes of evolution. Thus the elements nitrogen, oxygen, and fluorine will give rise to families of pentavalent, hexavalent,

and heptavalent elements respectively.

The three indirect derivatives of silicon, viz., vanadium, chromium, and manganese, are penta-, hexa-, and heptavalent, but they differ very considerably from the three elements nitrogen, oxygen, and fluorine, which have the same valencies. The three first mentioned elements are electro-positive, that is to say, the electrons in each case exhibit comparatively little desire to complete their systems of eight. This is an abnormal condition, and one that it is difficult to find any reason for. It may be owing to the fact that these elements have been produced by two indirect processes of evolution, or it may be owing to the size of the outer rings. That the three elements, vanadium, chromium, and manganese have practically no desire to complete their sets of eight is evidenced by the fact that they do not form any compounds with hydrogen or with any other electro-positive element. Although they are pentavalent, hexavalent, and heptavalent

respectively, yet these valencies are not usually exerted, the salts of these metals being due to the existence of secondary valencies of some form or other; in fact, the principal valencies are hardly exerted at all, consequently the direct derivatives in the process of evolution from these elements should be produced in much smaller quantities than in the case of the typically pentavalent, hexavalent, and heptavalent elements, nitrogen, oxygen, and fluorine. If we take the case of the elements vanadium and chromium, it will be seen that their direct derivatives which are placed under them in our Periodic Table occur much less frequently upon the earth than the two elements themselves.

In the case of manganese, we have a heptavalent element, which is the last possible indirect derivative of silicon, and we might point out that the heptavalency of this element is only exerted in the case of the heptoxide, which itself is only known in combination. Conversely we can argue that the tendency of the seven electrons of manganese to complete their system of eight is extraordinarily small. So small is this tendency that manganese is incapable of giving rise to any direct derivatives, that is to say, it has not the capability of adding on a complete ring and producing a heptavalent element more electro-positive than itself. Now the evolution process when it has arrived as far as the element manganese cannot stop, for manganese is a perfectly stable element, showing no sign of radio-activity, and consequently we must assume that the evolution process can and does proceed further. On the other hand, manganese cannot give rise to any indirect products of evolution such as we have described above, for when an indirect process of evolution takes place, an outer ring is produced with the transference of electrons numbering one less than those transferred in the direct process of evolution; inasmuch as the direct process of evolution from manganese would require the transference of one electron only, it is clearly impossible for a truly indirect evolution to take place, because this would mean the transference of no electron.

The oxides and halogen derivatives of manganese show, as before stated, that this element nearly always acts by secondary valencies and very rarely by its principal valency. We should therefore expect that any evolution derivatives of manganese should be peculiar and quite different from any which have previously occurred. The only thing that manganese can do is to add on very small quantities of matter, and give rise to substances with quite abnormal rings. Theoretically these rings should have a maximum valency of eight, that is to say, rings which could give rise to tetroxides

under certain conditions; at the same time, these rings should have extraordinary properties inasmuch as we can only view the evolution from manganese as being in the nature of plastering up its ring, so to speak. For these reasons, as well as from the facts of stellar evolution, we consider that iron, nickel, and cobalt are the products of this operation. Now the properties of the external rings of these elements are certainly very abnormal. These three elements are strongly magnetic and so we may look upon their rings as being to a certain extent plastic; that is to say, they are readily deformed under the influence of a magnetic field. It is perfectly true that none of these three elements shows the expected valency of eight, but in the elements ruthenium and osmium, which are the direct derivatives of iron, we do find evidences of this octo-valency. We would argue from this that the octovalent character is latent in the case of iron &c., that it becomes more pronounced in the case of ruthenium, which gives a tetroxide known in combination, and still more pronounced in the case of osmium, which gives a perfectly stable tetroxide.

It must be pointed out here that there is a very considerable difference between the octovalent ring of these elements and the saturated eight-membered ring of the elements belonging to the helium family. In the first case, we have a ring which can under suitable conditions give up eight electrons, but which prefers to act by secondary valencies, especially the valencies of two, three, and four. On the other hand, the rings of the elements of the helium family must be looked upon as saturated rings which have no power to act by

secondary valencies at all.

There is no doubt that the elements iron, nickel, cobalt, and other direct evolution products represent a somewhat unsatisfactory condition of affairs, and that each one of them will tend in the natural course of evolution to recover itself and form more or less ordinary derivatives. We think that the elements copper, zinc, gallium, and germanium, and the elements directly below them, represent these recovery products. That is to say, copper, zinc, gallium, and germanium are the successive recovery products of iron, nickel, and cobalt, while silver, cadmium, indium, and tin are the successive recovery products of ruthenium, rhodium, and palladium, and that gold, mercury, thallium, and lead are the successive recovery products from osmium, iridium, and platinum. We will return to this question of recovery again when dealing with the electropotential series of Professor Abegg.

In discussing the position of the four protons, viz., hydrogen, proto-beryllium, proto-boron, and helium, we placed helium at the head of the family of rare gases, saying that it acts as the progenitor of this family. Of course it is usually assumed from ordinary chemical evidence that these elements have no powers of entering into combination, and it might be argued from this that it would be impossible for helium to produce evolution products of its own type. Unless, however, we make the somewhat unjustifiable assumption that the elements neon, argon, krypton, and xenon are entirely devolution products of some radioactive processes, we must assume that they possess some form of residual valency. It is quite true that no definite evidence of this residual valency has yet been proved by our somewhat crude methods of chemical observation. There is no doubt in our own minds that this residual valency does exist, and we are in great hopes that before very long some physical method may be found of determining its existence and its amount.

In connexion with the general scheme of evolution as set forth, a most interesting point arises which is well worth noticing. We have already stated that the tendency of the four electrons on the outer ring of the element silicon to complete the system of eight is very small, and that, consequently, the tendency to form direct derivatives will be relatively small. The tendency therefore of the element silicon to give rise to indirect processes of evolution will be relatively greater; and in this fact we have an explanation of why the indirect derivatives of silicon occur in so much greater quantities than the direct derivatives. The indirect derivatives to which we especially refer are manganese, iron,

nickel, cobalt, copper, and zinc.

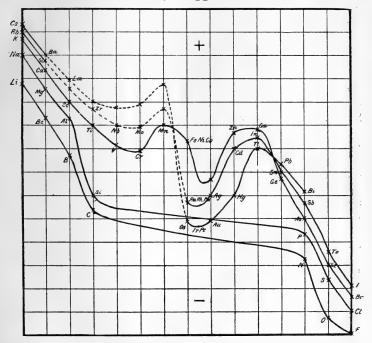
There is one most important aspect of any evolution process which must not be forgotten. As stated in our preliminary account on page 23, the whole process of evolution must of necessity be governed by the fact that evolution is attended by decrease of energy content, for it is perfectly clear that this is the fundamental law of physical or chemical change. If we consider any particular series in the Periodic Table, we should expect to find some evidence of this decrease of energy content. It is naturally impossible that we should be able to express in any way the actual energy content of any atom, but we can gain considerable information by making comparative measurements along any series. For example, if we take the series of the halogens, we find that the first member, fluorine, has very powerful chemical properties; that is to say, the desire to pick up electrons to complete the

set of eight is extraordinarily strong in this element. In other

words, it is exceptionally "electro-negative."

If we take the next element chlorine, we find the same properties, but to a less degree, and following through bromine to iodine, this desire to enter into combination decreases. This fall in electro-negative behaviour may be considered as being due to the fact that as the evolution progresses a more and more dense system is formed: that is to say, more and more energy escapes.

Now Professor Abegg \* has published a most important Table of the Values of the Electro-potentials of the Elements, and from this we can see at once that the tendency of the elements to take up electrons always falls as the direct process of evolution progresses, that is to say, the electro-positivity rises precisely as we should expect, if our theory is to hold good. We give a diagram showing Abegg's values, which is modified



slightly so as to show more conveniently the relations between the families in our Periodic Table. It can at once be seen that the values of the potentials as given by Abegg do not fit in with the Periodic Table as usually adopted at the present time. They do, however, agree much better with the groupings of the

<sup>\*</sup> Zeit. Anorg. Chem. 1904, xxxix. p. 330.

elements set forth in our Table. A most interesting point arises in connexion with the potentials of those elements which arise from manganese. We have shown above that the element manganese first gives rise to iron, nickel, and cobalt, whose outer rings theoretically are octovalent. This is accompanied by a considerable fall in the value of the potentials. This is a perfectly natural sequence, because it is quite evident that elements possessing this type of octovalent ring should show considerably decreased affinity, or, in other

words, that their electro-potentials should be small.

Now we pointed out that this octovalent ring must not be looked upon as being completely established in the case of iron, nickel, and cobalt, and that it becomes more established as the normal evolution proceeds through ruthenium &c., to osmium &c. This establishment of the octovalent character is naturally accompanied by a still further fall in value of the potential. When the recovery occurs from iron, nickel, and cobalt, to copper, the value of the potential falls to a minimum and then rises again to copper, and a still further rise occurs when the evolution proceeds to zinc, and again to gallium. A similar rise in the potential takes place when the recovery passes from ruthenium, rhodium, and palladium through silver and cadmium to indium, and again from osmium, iridium and platinum, gold, and mercury, to thallium.

It will be noticed that the recovery from ruthenium, rhodium, and palladium is steeper than the recovery from iron, nickel, and cobalt, and further, that the recovery from osmium, iridium, and platinum is even steeper still. result is that the three recovery curves cross one another after passing through gallium, indium, and thallium before they arrive at lead, tin, and germanium. At first sight it might be expected that the three elements germanium, lead, and tin should have a higher value of potential than gallium, indium, and thallium respectively; but it must be remembered that the three former elements are tetravalent, that is to say, the tendency of the four electrons to enter into combination is distinctly less than in the case of the gallium, indium, and thallium triads. The values of the electric potentials therefore of lead, tin, and germanium should be less than those of gallium, indium, and thallium.

We may point out that this accounts for the fact that the electric potentials of the three groups, copper, silver and gold, zinc, cadmium and mercury, gallium, indium and thallium are inverted. It is for this very reason that we do not consider these three groups to consist of normally developed elements, that silver and gold, for example, are

not direct evolution products of copper. In support of our view that the individual members of these three groups are not connected by a process of direct evolution, we would also mention that the three elements zinc, cadmium, and mercury have been shown by Cuthbertson and Metcalfe \* not to be connected in their refractivities.

A remarkable result has recently been obtained by J. J. Thomson t, which is entirely in agreement with the theory of evolution as set forth above. He has found that the number of corpuscles in an atom approximates to the atomic weight. Thus in the atom of hydrogen there is 1 corpuscle, and in a molecule of air there are 25-28. Now, with our hydrogen is associated 1 electron, with nitrogen 8+5=13 and oxygen 8+6=14, which would give about 27 to 1 molecule of air. Can it be these free electrons which have been measured? The objection to the result is that there are many more lines in the arc spectrum of iron which give the Zeeman effect, than there would be electrons. However, when subjected to the great strain of the electric arc, it is highly probable that some of the corpuscles from the outer ring of the atom are set into vibration, as well as the electrons, and this would afford an explanation of the number of lines.

However, to return to our main subject. We have traced the growth of all the elements, and will now proceed to

discuss the relations of their properties.

Firstly, members of the same family are formed from the same protons, and have the same shaped rings. Hence there must be a very close relationship in all their properties, as is the case in groups 1, 2, 3, and 8, where the structure is perfectly regular. Groups 5, 6, and 7 are also very similar; but the first members differ somewhat from the others, because the first ring is situated round one of different valency, or shape.

Again, on the outer ring will depend a certain number of properties. Two elements with the same outer ring will show several similarities. Their spectra will probably be of the same type, and their valencies being the same, they will form

similar compounds.

Now Rudorf  $\ddagger$  obtained certain relations between frequency differences of pairs of lines in the spectrum of an element and its atomic weight. On plotting the values of  $d/A^2$  against those of A, where d is the frequency difference for an element of atomic weight A, he obtained characteristic curves for each family; moreover, the point representing sodium was at the intersection of the curves through K, Cs, Rb, and Cu, Ag, Au.

<sup>\*</sup> Loc. cit.

<sup>†</sup> Phil. Mag. vol. xi. p. 769 (June 1906). ‡ Zeits. Phys. Chem. vol. 50. p. 100 (1904).

Consequently, spectroscopically, sodium belongs to both these families, a fact which confirms our supposition. Precisely

the same holds in the case of magnesium.

Copper affords an example of special interest. As above, its spectrum is seen to resemble that of sodium, but there are also lines which are similar in type to those of tin, lead, and some other heavy metals. The explanation of this fact is that the outer copper ring is of the same shape as the outer sodium ring, but yet the internal structure of the two is different, that of copper being similar to tin and lead.

The properties of an element will, however, not depend solely on its outer ring, but also upon two other main causes. These are (a) the actual number of rings in an atom, and (b) the way in which the rings are superimposed on each other.

The effect of the first cause upon the properties of the atom is simply that the larger the number of rings, the more unstable the atom, or we may perhaps say, the greater its tendency to disintegration. The second cause has been already touched on; it may be mentioned, however, that wherever a whole atom is composed of rings of the same kind, the outer ring will behave normally; but where the rings are not of the same kind, there will be what may be looked upon as distortion, and consequently abnormal properties are to be expected, and the greater the valency of a ring the more marked the distortion will be when such a ring is superimposed on one dissimilar to itself.

We are now in a position to discuss the influence of the constitution of the elements on their chemical reactions. We will, for the sake of clearness, limit ourselves mostly to simple

combinations of two elements.

Chemical compounds are formed entirely by an exchange of electrons between the combining atoms; but the number of electrons taking part in the exchange, and the ease with which they do so, depends on the structure of the atom.

As before stated, the chief tendency of the electrons is to form into systems of eight, and when this occurs, what may be called the principal valency is exerted. As an example, calcium with two electrons will give them up to oxygen which has six; when this occurs the calcium will become positively, and the oxygen negatively charged with "electricity," and combination results. To secure uniformity we may say that in this change calcium is divalent and oxygen hexavalent, the principal valency being the number of electrons the atom can give, or eight minus the number it can receive. Thus nitrogen will take three electrons from hydrogen, or give five to oxygen, being in both cases pentavalent. Simple changes such as the above always take place

in such a way that the number of electrons transferred is a minimum; so, with sodium and chlorine, the sodium will give one electron to the chlorine, and not receive seven from it. That this is so, is evident from the following considerations. Given that a system of either eight or zero electrons round an element is the most stable, an element with seven electrons, or with one only, is very near the stable position. the first case, the element with seven electrons will very readily acquire another; and in the second case, the element with only one will very readily give it up. So also an element with two electrons will readily lose them, but not so readily as an element with only one; three electrons will be lost or gained still less readily; and finally, in the case of an element with four electrons, it is a matter of indifference whether others are gained or lost. In other words, monovalent elements may be said to be, in general, the most electropositive, heptavalent the most electronegative, and tetravalent ones to be electrically neutral.

Loss or gain of electrons, according to the above idea, constitutes the principal valency of an element, and it must be noted that more than four electrons never leave or approach one element, and that, moreover, unless the outer ring is

highly distorted, there is only one principal valency.

Now in addition an element may have secondary valencies. This idea is due to Abegg, but he assumes that each element has one principal and one secondary valency, and that the sum of these is eight. Also in the first three groups the secondary valency is latent. It seems more reasonable to suppose that an element may have more than one secondary valency, and apparently these secondary valencies are either all even or all odd. If this be so, we may tabulate the number of electrons which any given ring will lose or take, bearing in mind that there is only one principal valency. Thus:

A monovalent	ring	will	lose	. 1	electron	or acquire	1, 3, 5, or 7.
A divalent	,,	,,		$^2$	. ,,	,,	2, 4, or 6.
A trivalent	,,	,,		3	,	99°.	3 or 5.
A tetravalent	29	,,		2 or 4	. ,,	,,	2 or 4.
A pentavalent	,,	,,		3 or 5	,,	,,	3.
A hexavalent	,,	,,		2, 4, or 6	,,	,,	2.
A heptavalent	"	,,		1, 3, 5, or <b>7</b>	, ,,	,,	1.
An octovalent	,,	,,		0	,,	,,	0.

In this it will be noticed that the tetravalent ring has no principal valency, and this would be expected, since it is the connecting link between elements with positive and negative principal valencies.

In accordance with the principle of minimum movement of electrons, it will be seen that when an element has several secondary valencies, it will for preference exert that which involves the least interchange of electrons. An excellent example of this is afforded by the halogens. These elements form the following compounds among themselves:—IF<sub>5</sub>, ICl<sub>3</sub>, and IBr; BrF<sub>3</sub> and BrCl. Fluorine is electronegative enough to make iodine give up five electrons, chlorine will only make it give three, and bromine can extract one only. So, bromine will give three to fluorine, but only one to chlorine.

Now it has been already pointed out that if the atom is built up of rings of different valency, or, in other words, is deranged, the properties will be affected, and consequently the above statements as to valency will not rigidly hold in such cases. A typical example of this is afforded by nitrogen, where there is a pentad ring on a triad. Here the principal valency is unaltered, being five, and five only, as nitrogen will take up only three electrons from hydrogen to form NH and NH<sub>2</sub> are not known. The secondary valencies are, however, affected, with the result that nitrogen can lose either two or four electrons in NO and NO<sub>2</sub>. similar state of affairs exists with vanadium, chromium, and manganese, where both even and odd valencies are found.

The next thing is to consider the valency of the elements normally derived from the above. It would naturally be supposed that, as these elements add on rings of the same valency as the outer one of the elements from which they are derived, their structure would tend to become more regular, and this is found to be so with nitrogen, oxygen, and fluorine We should expect this influence to be best evidenced in the cases of antimony, tellurium, and iodine; and it is undoubtedly shown by the compounds of these three elements, Sb<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>5</sub>; TeO, TeO<sub>2</sub>, TeO<sub>3</sub>; IBr, ICl<sub>3</sub>, I<sub>2</sub>O<sub>5</sub>, and  $I_2O_7$  (in compounds). Here, antimony exerts the secondary valencies of 3 and 5, tellurium of 2, 4, and 6, and iodine of 1, 3, 5, and 7, so that they have become perfectly normal. The intermediate elements are in a state of transition so to speak, and therefore nothing can be definitely argued from them.

In vanadium and chromium derivatives, however, there is practically a double derangement, since in the first place carbon is deranged (tetrad on triad), and then either a pentaor hexavalent ring is added to the tetravalent ring of silicon. The result is that these elements do possess even and odd valencies; for example, molybdenum forms MoCl<sub>2</sub>, MoCl<sub>3</sub>, MoCl<sub>4</sub>, MoCl<sub>5</sub>, and probably MoCl<sub>6</sub>.

In the series carbon, silicon, titanium, zirconium, there is only one derangement, and consequently, only even valencies are found.

Before concluding this section of our paper, it might be as well to make a few remarks on the rare earth elements. It will be seen that we have assigned positions between cerium and tantalum to those which are known definitely. According to our theory, their resemblance is due to a special characteristic trivalent ring, which largely masks any other properties resulting from internal structure. since so little is known of them chemically, it is unsafe to say whether we are justified or not. There are, however, three of them about which a little more is known, viz. praseodymium, neodymium, and samarium. Emerson Reynolds \* has given several good reasons for supposing them to belong to the iron group. One of these is the high paramagnetic susceptibility of their salts. Now we have already stated that the iron group is especially characterized by the magnetic properties of its first three elements, which arise from the presence of an abnormal ring. As evolution proceeds, this ring is not destroyed, but still exists inside the atom, and hence by our theory we should expect the derivatives of the first three elements to exhibit this particular property, but to a less degree. So, if it is granted that these three elements may be placed among the platinum metals from which they at first sight differ so greatly, it is to be hoped that no objection will be taken to the more or less temporary positions we have assigned to the others.

We have now discussed our theory of the method of growth of the atoms, and if our surmise is correct, would it not be reasonable to suppose that the table of atomic weights as rearranged would exhibit some quantitative relations between the weights of the atoms of the elements? If the atomic weights of the elements of group I are written down in order, and each subtracted from the one that comes after it, the following numbers result:—

6.02 16.02 16.01 46.3 47.4,

and these numbers may be regarded as the weights of the outer rings of the elements from lithium to exsium.

Examining the other groups, it is found that in general the differences are again 6, 16, and some number between 40 and 50; but whereas all the numbers belonging to the first class are very nearly 6 or 16, and that though the other numbers vary considerably, they approximate to a mean value of 46, showing a definite repetition and relationship between them. If we again consider the numbers 6, 16, resulting from group I., we note that they may be written:

(1+2+3), and (1+2+3)+(1+2+3+4)

respectively.

<sup>\*</sup> Chem. Soc. Journ. vol. lxxxii. p. 619 (1902).

The next term of a series of natural numbers arranged in this way which approximates most closely to the average number 46 is—

$$(1+2+3)+(1+2+3+4)+(1+2+3+4+5)$$
  
  $+(1+2+3+4+5+6) = 52.$ 

Now the average value of the differences is, as we have seen, approximately 46, a considerable diminution from the figure as given by the above series. In connexion with this, it is worthy of note that Runge and Precht \* determined the atomic weight of radium spectroscopically, and found it to be 258, while the value found by chemical methods was 225. Rudorf †, in seeking to explain the discrepancy, made a series of observations upon the relation between the frequency differences of spectral lines of families of elements. He found that if d is the frequency difference of pairs of lines in the spectrum of an element atomic weight A,  $d/A^2$  is approximately constant for low values of A, but increases with A for higher values of A. This means that the elements towards the end of the series have a lower atomic weight than would be the case if the formula  $d/A^2$  = constant were rigid.

The phenomenon appeared in all the series of elements

which were examined, and not only in group II.

Thus we have another example of a formula yielding higher values for the atomic weights than those actually found. May it not be that these formulæ give the atomic weights which the elements would naturally assume if not subject to some disturbing influence? In other words, is it unreasonable to suppose that we are here face to face with the process of devolution?

We know that this process exists in a marked form in the later stages of each group, in the form of radioactivity. Is it illogical to postulate that its origin occurred at an earlier

stage in the growth of the element?

If we may regard the formation of the elements as a combination of the processes of evolution and devolution, the former is most effective among the first elements of a group,

and the latter among the last.

Turning to devolution, and again examining the table of atomic weights, it is evident that there is no simple law connecting the various elements of high atomic weight, such as exists for the evolution. Moreover, since any term of the series of devolution is only obtainable when the difference of the atomic weights of two consecutive elements in any group

<sup>\*</sup> Phys. Zeitschr. vol. iv. p. 285 (1903). † Zeit. Phys. Chem. vol. 50. p. 100 (1904).

is known, and owing to the many uncertainties which exist in the atomic weights of the elements, and the number of them which are not yet discovered, it is exceedingly difficult to obtain even an approximation to a law for devolution,

However, there is one group which is fairly complete, viz. group II., and if any law is to be derived, it is naturally to

this group that we should look for information.

The atomic weights of the members of this family are as follows:—

Proto-beryllium between	1 and 4
Beryllium	
Magnesium	24.3
Calcium	40.1
Strontium	87.6
Barium	
Proto-radium	169-172?
Radium	225

The differences between these weights taken in order, omitting proto-beryllium for the present, are:—

Beryllium to magnesium	15.2
Magnesium to calcium	15.8
Calcium to strontium	47.6
Strontium to barium	49.8
Barium to proto-radium, about	34
Proto-radium to radium, about	52

If we subtract the numbers given by the series, which correspond to the above values (namely 16 and 52), from these values, we obtain the following numbers:—

Beryllium to magnesium	-0.8
Magnesium to calcium	
Calcium to strontium	-4.4
Strontium to barium	-2.2
Barium to proto-radium, about	-18
Proto-radium to radium, about	0

It will be observed in the foregoing numbers, that alternate members -0.8, -4.4, -18, form a descending series; and if we treat other groups of elements in the same way, their alternate numbers also invariably form descending series, but, as before mentioned, the number of members in these groups being incomplete, we can only observe the above-mentioned fact, and are unable to deduce any mathematical formula in their case.

Returning to the series -0.8, -4.4, -18, it is evident that this represents the devolution from the standard series 6, 16, 52. Let us now consider the remaining terms of the series, namely -0.2, -2.2, and 0.

These may be expressed in the form -0.8 + 0.6, -4.4 + 2.2, -18 + 18, and may thus be regarded as a growth, or recovery from the values given above for the devolution of the elements of group II. To be more explicit, we may say that alternate members of group II. are subject first to a period of evolution, and then of devolution, and that the remaining elements of this group are subject to both these influences and, in addition, a further return of evolution.

A close approximation for the two series -0.8, -4.4, -18, and 0.6, 2.2, 18, may be written as follows:—

	Loss.	Reco	very.
$2^{0}$	(1.1)	$2^{0^2}$	(1.1)
$2^2$	(1.1)	$2^{12}$	(1.1)
$2^4$	(1.1)	$2^{2^2}$	(1.1)

The general expression for the loss if written as above is

$$\frac{11}{10} 2^{(p-2)}$$
 where  $p=2, 4, \text{ or } 6$ ;

or, in other words, is the position of the corresponding element in the original series.

The general expression for the loss and recovery of the

odd members is

$$\frac{11}{10} 2^{(p-3)} - \frac{11}{10} 2^{(\frac{p-3}{2})^2}$$
 where  $p = 1, 3, 5, \text{ or } 7,$ 

these numbers denoting position in the series as above.

Returning to the original series for the evolution, viz., 6, 16, 52, the general term may be written in the form

$$\frac{(2+2)(2+3)(2+4)-4!}{3!};$$

where n=1 for the first row of the table, 2 for the next two rows, and 3 for the last four.

Thus the complete formula for the evolution and devolution of group II. is

$$(\frac{2+2)(2+3)(2+4)-4!}{3!} - \frac{11}{10} 2^{(p-2)}$$

for the even members, and

$$\frac{\binom{n-1}{2}\binom{n-1}{2+3}\binom{n-1}{2+4}-4!}{3!}-\frac{11}{10}2^{\binom{p-3}{2}}+\frac{11}{10}2^{\binom{p-3}{2}}^2$$

for the odd.

If we employ this formula, reckoning differences from calcium as standard, we obtain the following values for the atomic weights of group II., and may compare them with those given in the international table:—

Element. Proto-beryllium	Value from formula. 1·3	International value.
Beryllium	9.2	9.1
Magnesium	24.1	24.36
Calcium	40.1	40.1
Strontium	87.7	87.6
Barium	137.5	137.4
Proto-radium (Thulium?)	171.9	171
Radium	223.9	225

It is noteworthy that the value obtained by the foregoing formula for the element which precedes radium is 171.9. This is in close agreement with the usually accepted value for thulium, and thus substantiates the position in which we have placed it. In addition, putting p=1 and n=1, we obtain the value 1.3 for the atomic weight of the element preceding beryllium. This is in agreement with the fact that this weight should lie between 1 and 4, and the actual value is probable, when viewed in the light of considerations which are to follow.

Before proceeding we may draw attention to some interesting facts concerning our original series for evolution, viz., 6, 16, 52, or as we wrote it:—

$$6 = (1+2+3)$$

$$16 = (1+2+3) + (1+2+3+4)$$

$$52 = (1+2+3) + (1+2+3+4) + (1+2+3+4+5)$$

$$+ (1+2+3+4+5+6).$$

There is one term of 6, two of 16, and four of 52, but in the growth of the elements as shown by the table, there is one growth of 6, two of 16, and four of 52.

Moreover, in term 1 there are three digits, and though in the first row of our table there are four elements, yet of these only three are electrically valent.

Again in term 2 there are seven digits, and seven electrically valent elements in the next two rows of the table.

In term 3 there are eighteen digits, and in the last rows of the table there are seventeen electrically valent elements, and this perhaps points to a relationship between the number of the digits in the above series, and number of electrically valent elements, in the corresponding rows of the table.

Stating this in another manner, the increase in the number *Phil. Mag. S. 6.* Vol. 15. No. 85. *Jan.* 1908.

of digits from the second term to the third is eleven, which is the number of elements to which silicon gives rise.

With reference to the rise and fall which we have developed in our mathematical equation as shown above, we would point out that if there is any real basis for this phenomenon, it must be exhibited in the properties of the elements concerned. That there is indeed a very striking connexion is clearly shown in the following Table of oxides and chlorides which are known to exist for the elements of the nitrogen, oxygen, and fluorine groups:—

$NCl_3$	$P Cl_3$	$As Cl_3$	$Sb Cl_3$	Bi Cl <sub>3</sub>
-	$P Cl_5$	-	Sb Cl <sub>5</sub>	_
	$S Cl_2$		${ m Te}\ { m Cl}_{_2}$	
	$\mathrm{S}$ $\mathrm{Cl}_4$	$\operatorname{Se} \operatorname{Cl}_4$	$\mathrm{Te}\;\mathrm{Cl}_4$	
	$SO_2$	$Se O_2$	${ m Te}~{ m O}_2$	
	$SO_3$		${\rm Te}~{\rm O}_{_3}$	
	${ m Cl}~{ m OH}$	$\operatorname{Br}\operatorname{OH}$	IOH	
	Cl O OH	_	I Cl <sub>3</sub>	
	$\text{Cl O}_2\text{OH}$	$\operatorname{Br} \operatorname{O}_{\scriptscriptstyle 2}\mathrm{OH}$	$I O_2OH$	
	$\text{Cl O}_3\text{OH}$	_	$IO_3OH$	

Moreover, since the members of the first three groups do not commonly exert more than one valency, we cannot expect to find any phenomenon analogous to the above in their case. Also in the silicon family the sub-groups are too small to show the same, and consequently any rise and fall in affinity as shown by variable valency should only be looked for in the nitrogen, oxygen, and fluorine groups, and it is precisely here it does occur. From this it appears that the alternate members of these groups, viz., nitrogen, arsenic, bismuth, selenium, and bromine, do not exert their valencies to such an extent as the remaining elements. The pentachlorides of nitrogen, arsenic, and bismuth do not exist, and though As<sub>2</sub>O<sub>5</sub> is known, it is much less stable than P<sub>2</sub>O<sub>5</sub> or Sb<sub>2</sub>O<sub>5</sub>. Again, selenium is only tetravalent in its simple compounds with oxygen and chlorine, whereas the other members of its family are divalent, tetravalent, and hexavalent as well. The selenates with hexavalent selenium exist, but are comparatively unstable. Finally, in the halogen family, no compounds of bromine are known in which this element is tri- or heptavalent.

While offering no explanation for this phenomenon, we think that it is at least highly interesting, especially when viewed in the light of the rise and fall in atomic weight given

by our formula.

We would further point out that the maximum fall occurs in the case of the rare earth thulium in the second group.

That is to say, this element has been formed with a considerable fall in atomic weight from its theoretical value. We have endeavoured to derive expressions for the atomic weights of all the other groups of elements, but we have not been entirely successful owing to the want of knowledge of the atomic weights of the highest members. We find, however, that the same periodic phenomenon of rise and fall takes place in all the groups, and moreover that a rare earth element always appears at the position of the maximum fall. This fact is an experimentally suggestive one in connexion with the phenomenon of radioactivity. Now the chemical properties of the rare earths are apparently extremely complex. The fact that all these substances are trivalent we attribute to the fact that they possess an outer trivalent ring. Of the internal structure of the atom in each case it is impossible to speak with any certainty: in fact there is little doubt that these substances are quite abnormal.

Now inasmuch as these elements are produced at a period of maximum fall in the evolution of each family, it would appear that they are the result of the degradation of substances of higher atomic weight. It does not seem far from improbable that the final degradation products of all radio-

active elements should be a rare earth.

In the last section of our paper we introduced the idea of a process of devolution, and the natural result of such an idea is an inquiry as to whether the structure which we assigned to the atoms to account for their evolution will also account for what is known of their devolution. As before mentioned, we have undoubted cases of devolution in the radioactive bodies, and a large number of most interesting facts have recently been observed in connexion with them

by many workers.

Of all these facts, perhaps the most interesting, from our point of view, is that the mass of the Alpha particles of radium, uranium, thorium, and actinium have been found to lie between the masses of the atoms of hydrogen and helium. Now in developing our theory of evolution we laid great stress upon what we described as the principle of "heredity" in normal direct evolution; that is to say, we consider for example that the outer rings of the elements, with the exception of thulium, in the second group, are of the same shape, viz., that shape corresponding to the valency of two. Perhaps our meaning in this connexion might be rendered clearer by taking an analogy with crystallization. When a solution of a salt is sown with the proper form of crystal, the salt proceeds to crystallize out along the lines which have been as it were laid down for it. Although perhaps

this analogy is not very good, yet it does more or less express our meaning, for we might consider that the element proto-beryllium acts as it were as a seed, and its evolution products grow from it, preserving very much the same shape and characteristics. We do not necessarily mean that the successive products of evolution are merely magnified products of the original antecedent, but rather that each evolution product consists of groups of nuclei, each nucleus having the shape of the original antecedent element, proto-

beryllium.

On these grounds, it is not unreasonable to suppose that if in the process of evolution an unstable element were produced it would break down and give off one or more of these nuclei. This nucleus would have a mass equal to that of the original antecedent element. It is these nuclei which in our opinion determine the particles. As mentioned previously, we believe that the atomic weight of proto-beryllium and proto-boron lies between 1 and 4, and this does not differ from the results. so far obtained for the mass of the particles. If it be granted that an a particle is a proton, we can trace the change through which an atom formed according to our theory would go. For example, let us consider the case of radium. The atom is approximately 224 times the weight of a hydrogen atom. and has been evolved from an element having an atomic weight not far from 1.3. That is to say, the outer ring of the element radium could be looked upon as being composed of nuclei, each nucleus being, by our principle of "heredity," of the same type and shape as that of the original element proto-beryllium. Now this element, radium, is unstable. It proceeds to lose one of its nuclei. The whole of the remaining atom will then seek to find the next position of stability. It might take the position of the last element in group I., but this would be no more stable than its original position; and so it seeks to establish itself in group VIII, forming the emanation. Now when the  $\alpha$  particle, which we believe becomes an atom of proto-beryllium, leaves the atom of radium, the outer ring of radium is left with groups of eight electrons. That is to say, in so far as its outer ring only is concerned, the emanation belongs to the helium family. Now this emanation again proves to be an unstable atom, possibly owing to the fact that its outer ring is of quite a different type to the inner ones. It again breaks down giving up more a particles. Now inasmuch as the outer ring of the emanation is of the helium type, so the particles are helium atoms.

So, when radium turns to the emanation the proto-beryllium protons must turn into helium protons. The single corpuscles are probably not deranged during the transformation, since none are given out; hence we may assume that the only change which takes place is in the protons, and that this is of the nature of polymerization. Consequently, an integral number of radium protons must form the atom of helium, and if this be so, the atomic weight of the proto-beryllium proton must be 1.33 or 2, so that either three, or two of them, unite to form helium.

Now the value given by our formula in the last section, for the atomic weight of proto-beryllium, was 1·3; moreover, we are about to show that there are reasons for believing that the atomic weight of proto-boron is 2, and consequently we must assume that the atomic weight of proto-beryllium is 1·33. We will now consider the behaviour of thorium and actinium. These elements resemble each other in their method of disintegration, and consequently they may be treated together.

By thorium, we mean the element which gives rise to

thorium X, its emanation, and its active deposit.

In the cases of thorium and actinium, we have two heavy atoms, in all probability heavier even than radium, and composed of proto-boron protons. When one of these particles is expelled, the atom, as in the case of radium, will try to assume a more stable form. Now since the rare earths are all formed by the preceding elements adding a trivalent ring, it appears that such a ring is at any rate a configuration of great stability, and it should not surprise us if an element when disintegrating should form a stable derivative with a trivalent ring, and that this is the X derivative. In other words, thorium and actinium will have been transformed into thorium X, and actinium X, with trivalent outer rings, but they will have the same sized a particles, as their protons have as yet undergone no change. If this is the case, we can see why thorium, actinium, and uranium should form thorium X, actinium X, and uranium X, while radium should be immediately transformed into its emanation weight of radium being below that of the element which would occupy the last position of group III., radium in the process of devolution cannot turn into this element, but goes at once into the helium family. The other elements have a higher atomic weight, and do form this element as they decay. This involves the fact that all the X's are the same substance, and we hope at a future date to give reasons for believing that this assumption is correct.

The X elements when formed will give off an  $\alpha$  particle, and, like radium, become members of the helium family. By a method of reasoning similar to that in the case of radium,

it is highly probable that an exact number of proto-boron atoms will form one helium atom. Consequently, the atomic weight of proto-boron must be 1.33 or 2. But proto-boron is of necessity heavier than proto-beryllium, and consequently its atomic weight must be 2. Therefore, we see that the atomic weights of the four primary atoms form an harmonic series, namely 4/4, 4/3, 4/2, 4/1, which is interesting in connexion with Newland's original idea of octaves.

So little is known of the substances to which the various emanations give rise, that we will not hazard any suggestions

regarding them.

The last case before us is that of uranium, the simplest of all the radioactive elements. In this case, as with thorium and actinium, we have a heavy atom, heavier than radium, belonging to the carbon family. When one  $\alpha$  particle has been expelled, uranium, like thorium, changes into uranium X, but uranium X is very different to thorium X. Instead of giving out  $\alpha$  particles it gives out  $\beta$  and  $\gamma$  particles, and does

not decay into any emanation.

The mention of  $\beta$  and  $\gamma$  particles opens out an entirely fresh phase of radioactivity, and to explain it fully we should have to enter into many new details, which in themselves form sufficient material for a separate paper. However, as we mentioned at the commencement of our paper, the space at our disposal necessitated the omission of many astrophysical facts bearing directly upon the subject with which we have dealt, and now again we are constrained to pass over a fuller treatment of this important branch of radioactivity.

To recapitulate, our conclusions concerning the periodic law and radioactivity are direct deductions from stellar observations, and many other little understood facts connected with matter find an explanation in the same source. We chose the periodic law and an outline of radioactivity as being perhaps the most typical examples of this theory, but we hope to give others at no distant date, and also a more detailed account of the astrophysical observations which gave

rise to this paper.

In conclusion, we wish to express our most hearty thanks to Professor E. C. C. Baly and Mr. H. E. Watson for their valuable assistance, and the kind interest they have taken in this paper.

## EXPLANATION OF DIAGRAM (Plate VII.).

The diagram on Plate VII. represents what we believe to be the structure of elements of typical groups. Circles drawn at wide distances from each other (2 mm.) indicate regularity of structure, i.e. successive elements have the same valency. Circles drawn

more closely show where the structure is irregular. No meaning

is attached to the absolute size of the rings.

The figures indicate the valency of each ring, and consequently, the outermost figure of each element shows the number of electrons associated with it. 3' represents a rare earth ring, which, although drawn close to the ring next it, for the sake of distinction, produces no distortion in the element following it.

Group 3 only differs from group 2 by the fact that the rings are trivalent instead of divalent. The structure of the chromium group is the same as that of the vanadium group, but the pentavalent rings in the letter are replaced by hexavelent ones.

valent rings in the latter are replaced by hexavalent ones.

Manganese is the same as vanadium with a heptavalent outer

ring.

The only difference between iron, nickel, and cobalt, is in the mass of the incomplete dotted ring. The same holds for the remaining members of the iron group.

The three groups following copper have the same structure, but their outer rings are di-, tri-, and tetravalent respectively, instead

of monovalent.

Similarly, the structure of the oxygen and fluorine groups is the same as that of the nitrogen group, but the rings are hexaand heptavalent instead of pentavalent.

III. On the Curvature and Torsion of a Helix on any Cylinder, and on a Surface of Revolution. By L. V. Meadowcroft, B.A., M.Sc., Scholar of Trinity College, Cambridge \*.

In the following short paper I propose to discuss the curvature and torsion of a helix on any cylinder, and on a surface of revolution, by a new method. The method is of general application, and will apply to a helix on any surface. In this latter case, however, the formulæ are somewhat long and unwieldy; and so I have contented myself by simply indicating the method of procedure, without giving the analytical details in full. As far as I know the results are not new, but the method presents several points of novelty and interest.

I define a helix as a curve for which the ratio  $\frac{\rho}{\sigma}$  is constant,  $\rho$  and  $\sigma$  being the radii of curvature and torsion of the curve at any point. It follows, by a theorem given below, that the tangent and binormal at any point of the curve make fixed angles with a fixed straight line in space.

An equivalent definition is that a helix is a curve such that the tangent at any point of it makes a fixed angle with

a fixed straight line in space.

<sup>\*</sup> Communicated by the Author.

These two definitions may be proved to be equivalent by means of the following well-known theorems:—

Theorem 1.

If the tangent to a curve makes a constant angle  $\alpha$  with a fixed straight line in space, then  $\sigma = \rho \tan \alpha$ . Also the binormal makes the constant angle  $\frac{\pi}{2} - \alpha$  with the same straight line.

This is best proved by elementary geometry.

Theorem 2.

If the ratio  $\rho/\sigma$  be constant, the tangent-line and binormal

make constant angles with a fixed direction.

I shall give a proof of this theorem by means of Serret's Formulæ. Let (l, m, n) and  $(\lambda, \mu, \nu)$  be the direction cosines of the tangent and binormal at any point. Then by Serret's formulæ we have

$$\rho \frac{dl}{ds} + \sigma \frac{d\lambda}{ds} = 0, \quad \rho \frac{dm}{ds} + \sigma \frac{d\mu}{ds} = 0, \quad \rho \frac{dn}{ds} + \sigma \frac{d\nu}{ds} = 0.$$

: dividing each by  $\sigma$  and integrating, we get

$$\frac{\rho}{\sigma}l + \lambda = \text{constant} = A,$$

$$\frac{\rho}{\sigma}m + \mu = \text{constant} = B,$$

$$\frac{\rho}{\sigma}n + \nu = \text{constant} = C.$$

Multiply by 
$$\lambda$$
,  $\mu$ ,  $\nu$  and add:  $\therefore$   $A\lambda + B\mu + C\nu = 1$ .

Multiply by  $l$ ,  $m$ ,  $n$  and add:  $\therefore$   $Al + Bm + Cn = \frac{\rho}{\sigma}$ .

... the tangent line and binormal make fixed angles with the fixed direction  $\frac{A, B, C}{\sqrt{A^2 + B^2 + C^2}}$ , which proves the theorem.

Having proved the equivalence of the two definitions by means of these two theorems, it is permissable to use the properties which follow from both in the following work.

I take the fixed straight line as axis of z. Let  $\alpha$  be the constant angle made by the tangent line with the axis of z.

Then  $\frac{dz}{ds} = \cos \alpha = \text{constant}$ .  $\therefore \frac{d^2z}{ds^2} = 0$ .  $\therefore$  the principal normal is perpendicular to the axis of z, and so parallel to the plane of xy. Now the tangent line is perpendicular to the

principal normal, and the osculating plane contains the tangent and the principal normal. Hence it follows that the osculating plane at any point of a helix on any surface makes an angle  $\frac{\pi}{2} - \alpha$  with the plane of xy.

The simplest helix is that described on a circular cylinder. This is known as the common helix or spiral staircase. Its curvature and torsion can easily be found by several methods. I shall not consider this curve at all.

The first type of helix I shall discuss is that described on any cylinder, the axis of the cylinder being taken as axis of z.

In this case the tangent line makes an angle  $\alpha$  with the axis of z, and therefore with any generator. Hence the curve cuts the generators at the constant angle  $\alpha$ .

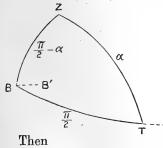
Then angle between the tangent-line and the axis  $=\alpha$ , and the angle between the binormal and the axis  $=\frac{\pi}{2}-\alpha$ .

Let P and Q be two neighbouring points on the curve, and let PQ=ds. Draw the generators through P and Q, and let the generator through Q cut the normal section of the cylinder through P in N.

Let  $\rho'$  be the radius of curvature of this normal section at P, and let  $d\phi$  be the angle

between the tangent planes to the cylinder at P and Q, i.e. at P and N.

Then  $PN = \rho' d\phi = ds \sin \alpha$ , from the figure.



Q

Draw a unit sphere with any point O as centre. Draw OZ parallel to the axis of the cylinder. Draw OB parallel to the binormal at P and OT parallel to the tangent line. Let B', T' be the points corresponding to the binormal and tangent line at Q.

$$ZB = ZB' = \frac{\pi}{2} - \alpha$$
,  $ZT = ZT' = \alpha$ ,  $BT = B'T' = \frac{\pi}{2}$ .

Now  $TT'=d\theta$  = the angle between the tangents to the curve at P and Q.

Also BB'= $d\eta$ =the angle between the binormals at P and Q.

Now 
$$d\theta = \sin \alpha \, d\phi, \\ d\eta = \cos \alpha \, d\phi,$$

since TZT'=BZB'=the angle between planes at P and Q, each containing the generator and the tangent line

= the angle between the tangent planes at P and Q, i. e. at P and N.

 $=d\phi$ .

$$\therefore \frac{1}{\rho} = \frac{d\theta}{ds} = \sin \alpha \frac{d\phi}{ds}$$
$$= \frac{\sin^2 \alpha}{\rho'}, \text{ since } ds = \frac{\rho' d\phi}{\sin \alpha}.$$

$$\therefore \quad \rho = \rho' \operatorname{cosec}^2 \alpha.$$

$$\frac{1}{\sigma} = \frac{d\eta}{ds} = \cos \alpha \frac{d\phi}{ds}$$

 $=\frac{\cos\alpha\sin\alpha}{\rho'}.$ 

 $\therefore \quad \sigma = \rho' \csc \alpha \sec \alpha.$ 

Hence  $\rho = \rho' \csc^2 \alpha, \\ \sigma = \rho' \csc \alpha \sec \alpha.$ 

Also  $\sigma = \rho \tan \alpha$ , as it should do.

Verification.

Again,

The usual method of procedure in such a case as the above is to project the helix onto the plane of xy, and find  $\rho'$  the radius of curvature of the plane curve. Let  $\gamma$  be the angle which the osculating plane at P makes with the plane of xy,  $\beta$  the angle made by the tangent at P with the same plane.

Then, by a general theorem,

$$\frac{\rho}{\rho'} = \frac{\cos \gamma}{\cos^3 \beta}.$$

In our case  $\gamma = \frac{\pi}{2} - \alpha$ ,  $\beta = \frac{\pi}{2} - \alpha$ ,

$$\therefore \quad \rho = \rho' \operatorname{cosec}^2 \alpha.$$

Also  $\sigma = \rho \tan \alpha$ , and

$$\therefore \quad \sigma = \rho' \csc \alpha \sec \alpha.$$

This verifies the above formulæ for  $\rho$  and  $\sigma$ .

Examples.

1. In the common helix,  $\rho'=a$  the radius of the circular section of the cylinder.

$$\begin{array}{ccc} \ddots & \rho = a \operatorname{cosec}^2 a, \\ \sigma = a \operatorname{cosec} \alpha \operatorname{sec} \alpha. \end{array}$$

These are well-known formulæ.

2. In an elliptic cylinder  $\rho' = \frac{a^2b^2}{p^3}$ , where p is the perpendicular from the axis onto the tangent plane at P, a and b being the semi-axes of the principal elliptic section of the cylinder.

$$\rho = \frac{a^2b^2}{p^3} \csc^2 \alpha,$$

$$\sigma = \frac{a^2b^2}{p^3} \csc \alpha \sec \alpha.$$

The next step is to apply the above method to find the curvature and torsion of a helix on any surface of revolution. As before, I shall take  $\alpha$  as the angle which the tangent at any point makes with the axis of z, and I shall further suppose that the axis of z is the axis of the surface. Let z=f(r) be the equation of the generating curve, r being the distance of any point from the axis.

Let P and Q be two neighbouring points on the helix, and

let PQ = ds.

Let the cylindrical coordinates of P and Q be  $(z, r, \phi)$  and  $(z+dz, r+dr, \phi+d\phi)$  respectively. Then

$$ds^2 = dz^2 + dr^2 + r^2 d\phi^2$$
.

 $\therefore dz^2 \sec^2 \alpha = dz^2 + dr^2 + r^2 d\phi^2, \text{ since } dz = ds \cos \alpha.$ 

:. 
$$dr^{2}[\tan^{2}\alpha \cdot f'(r)^{2}-1]=r^{2}d\phi^{2}$$
, since  $dz=f'(r)dr$ .

$$\therefore \frac{dr}{d\phi} = \pm \frac{r}{\sqrt{\tan^2 \alpha \cdot f'(r)^2 - 1}},$$

the + or - sign being taken according as r increases or decreases with  $\phi$ .

Draw the spherical diagram as before and let  $T\hat{Z}T' = d\omega$ . It will not now be equal to  $d\phi$ .

 $d\omega$  = the angle between a vertical plane at P containing the tangent line and the corresponding plane at Q.

Now the tangent plane at P makes an angle  $\psi$  with a

vertical plane perpendicular to the meridian plane at P,  $\psi$  being given by  $\tan \psi = \frac{dr}{dz} = \frac{1}{f'(r)}$ .

The tangent line at P lies in the tangent plane at P and makes an angle a with the vertical. It easily follows from this that  $\cos \chi = \tan \psi \cot \alpha$ ,  $\chi$  being the angle which the vertical plane containing the tangent line makes with the meridian plane through P.

At Q  $\chi$  will have the value  $\chi + d\chi$ , where

$$-\sin \chi \, d\chi = \sec^2 \psi \cot \alpha \, d\psi.$$

$$\therefore d\omega = d\phi + (\chi + d\chi) - \chi$$

$$= d\phi + d\chi$$

$$= d\phi - \frac{\sec^2 \psi \cot \alpha}{\sin \chi} d\psi.$$

Now

$$\tan \psi = \frac{1}{f'(r)}.$$

$$\therefore \sec^2 \psi \, d\psi = -\frac{f''(r)}{f'(r)^2} dr.$$

$$\therefore \sec^{2} \psi \, d\psi = -\frac{f''(r)}{f'(r)^{2}} dr.$$

$$\therefore d\omega = d\phi + \frac{\cot \alpha}{\sin \chi} \frac{f''(r)}{f'(r)^{2}} dr$$

$$= \pm \left[ \frac{\sqrt{\tan^{2} \alpha \cdot f'(r)^{2} - 1}}{r} + \frac{\cot \alpha}{\sqrt{1 - \tan^{2} \psi \cot^{2} \alpha}} \frac{f''(r)}{f'(r)^{2}} \right] dr$$

$$= \pm \frac{\tan^{2} \alpha f'(r)^{3} - f'(r) + rf''(r)}{rf'(r)\sqrt{\tan^{2} \alpha \cdot f'(r)^{2} - 1}} dr.$$

Now

$$\frac{1}{\rho} = \sin \alpha \frac{d\omega}{ds}$$

$$= \sin \alpha \frac{d\omega}{dr} \cdot \frac{dr}{dz} \cdot \frac{dz}{ds}$$

$$= \pm \sin \alpha \cdot \frac{\tan^2 \alpha f'(r)^3 - f'(r) + rf''(r)}{rf'(r)\sqrt{\tan^2 \alpha} \cdot f'(r)^2 - 1} \cdot \frac{1}{f'(r)} \cdot \cos \alpha.$$

$$\therefore \quad \rho = \pm \frac{rf'(r)^2 \sqrt{\tan^2 \alpha \cdot f'(r)^2 - 1}}{\tan^2 \alpha \cdot f'(r)^3 - f'(r) + rf''(r)} \cdot \frac{1}{\sin \alpha \cos \alpha}$$
Again,

$$\frac{1}{\sigma} = \cos \alpha \frac{d\omega}{ds}.$$

$$\therefore \quad \sigma = \pm \frac{rf'(r)^2 \sqrt{\tan^2 \alpha \cdot f'(r)^2 - 1}}{\tan^2 \alpha \cdot f'(r)^3 - f'(r) + rf''(r)} \cdot \frac{1}{\cos^2 \alpha}$$

Verification.

These formulæ for  $\rho$  and  $\sigma$  may be verified by the same method as was used in the verification for helices on cylindrical surfaces.

We have

$$ds^2 = dr^2 + dz^2 + r^2 d\phi^2.$$

This reduces, as above, to

$$\begin{split} dr^2 \big[ \tan^2 \alpha \cdot f'(r)^2 - 1 \big] &= r^2 d\phi^2. \\ \therefore & \tan^2 \alpha \cdot f'(r)^2 - 1 = r^2 \Big( \frac{d\phi}{dr} \Big)^2. \end{split}$$

Hence the p, r equation of the projection of the helix on the plane of xy is

$$\tan^{2}\alpha \cdot f'(r)^{2} - 1 = \frac{p^{2}}{r^{2} - p^{2}}.$$

$$\therefore p^{2} = r^{2} - \frac{-r^{2}}{\tan^{2}\alpha \cdot f'(r)^{2}}.$$

$$\therefore p \frac{dp}{dr} = r - \frac{rf'(r) - r^{2}f''(r)}{\tan^{2}\alpha \cdot f'(r)^{3}}$$

$$= r \left[ \frac{\tan^{2}\alpha \cdot f'(r)^{3} - f'(r) + rf''(r)}{\tan^{2}\alpha \cdot f'(r)^{3}} \right].$$

$$\therefore \rho' = r \frac{dr}{dp} = \frac{p \tan^{2}\alpha \cdot f'(r)^{3}}{\tan^{2}\alpha \cdot f'(r)^{3} - f'(r) + rf''(r)}.$$

$$\therefore \rho = \frac{\rho'}{\sin^{2}\alpha} = \pm \frac{r f'(r)^{2} \sqrt{\tan^{2}\alpha \cdot f'(r)^{2} - 1}}{\tan^{2}\alpha \cdot f'(r)^{3} - f'(r) + rf''(r)}. \frac{1}{\sin \alpha \cos \alpha}.$$

Also  $\sigma = \rho \tan \alpha$ ; and so we find  $\sigma$ .

These results verify the values of  $\rho$  and  $\sigma$  obtained by my method.

Examples.

1. Helix on a paraboloid of revolution.

Here  $z = \frac{r^2}{2l}$ , if l is the semi-latus rectum of the generating parabola.

 $f'(r) = \frac{r}{l}, \quad f''(r) = \frac{1}{l}$ 

Also r increases with  $\phi$ ; and so we take the plus signs in

62 Curvature and Torsion of a Helix on any Cylinder. the expressions for  $\rho$  and  $\sigma$ .

$$\therefore \quad \rho = \frac{r \cdot \frac{r^2}{l^2} \sqrt{\tan^2 \alpha \cdot \frac{r^2}{l^2} - 1}}{\tan^2 \alpha \cdot \frac{r^3}{l^3} - \frac{r}{l} + \frac{r}{l}} \frac{1}{\sin \alpha \cos \alpha} = \frac{\sqrt{r^2 - l^2 \cot^2 \alpha}}{\sin^2 \alpha}.$$

 $\therefore \rho^2 \sin^4 \alpha = \sigma^2 \sin^2 \alpha \cos^2 \alpha = r^2 - l^2 \cot^2 \alpha.$ 

This is a known result.

2. Helix on a sphere.

Here 
$$z = \sqrt{a^2 - r^2}$$
.  

$$\therefore f'(r) = -\frac{r}{z}, \quad f''(r) = -\frac{a^2}{z^3}.$$

If we take z to be positive  $\frac{dr}{d\phi}$  is negative.

$$\therefore \rho = \frac{-r \cdot \frac{r^2}{z^2} \sqrt{\tan^2 \alpha \cdot \frac{r^2}{z^2} - 1}}{-\tan^2 \alpha \cdot \frac{r^3}{z^3} + \frac{r}{z} - \frac{ra^2}{z^3}} \cdot \frac{1}{\sin \alpha \cos \alpha}$$

$$= \frac{\sqrt{r^2 - a^2 \cos^2 \alpha}}{\sin \alpha}, \text{ on reduction.}$$

$$\therefore \quad \rho = \frac{\sqrt{r^2 - a^2 \cos^2 \alpha}}{\sin \alpha}.$$
 Similarly 
$$\sigma = \frac{\sqrt{r^2 - a^2 \cos^2 \alpha}}{\cos \alpha}.$$

This again is a known result.

3. Helix on a cone of semivertical angle  $\beta$ .

Here  $z = r \cot \beta$ .

$$\therefore f'(r) = \cot \beta, \quad f''(r) = 0.$$

Also  $\frac{dr}{d\phi}$  is positive if the vertex be pointing downwards.

$$\therefore \quad \rho = \frac{r \cot^2 \beta \sqrt{\tan^2 \alpha \cot^2 \beta - 1}}{\tan^2 \alpha \cdot \cot^3 \beta - \cot \beta} \cdot \frac{1}{\sin \alpha \cos \alpha}$$

$$\frac{1}{\rho^2} = \frac{(\tan^2\alpha \cot^2\beta - 1)}{r^2 \cot^2\beta} \sin^2\alpha \cos^2\alpha = \frac{1}{r^2} (\tan^2\alpha - \tan^2\beta) \sin^2\alpha \cos^2\alpha.$$

Now it can easily be shown that a helix on a cone cuts all the generators at a constant angle  $\omega$ , where  $\cos \omega = \frac{\cos \alpha}{\cos \beta}$ .

$$\therefore \frac{1}{\rho^2} = \frac{\sin^2 \alpha \cos^2 \alpha}{r^2} \cdot \frac{\cos^2 \beta - \cos^2 \alpha}{\cos^2 \alpha \cos^2 \beta}$$
$$= \frac{\sin^2 \alpha \sin^2 \omega}{r^2}.$$

 $\therefore \quad \rho = r \csc \alpha \csc \omega.$ 

Similarly  $\sigma = r \sec \alpha \csc \omega$ .

This, again, is a known result.

Apparently the above method would apply to a helix on any form of surface, but the results would be too complicated to be of any use, except in very special cases. The only difficulty is to find  $d\omega$ . The tangent line at any point P makes an angle  $\alpha$  with OZ and lies in a known plane, i. e. the tangent plane at P. It might be possible to calculate from this the angle made by the vertical plane containing the tangent at P with (say) the plane x=0. Say this angle was found to be  $\psi$ . Then  $d\omega = d\psi$ ; but unless the surface was of a very simple nature, the results would be useless because of their length and want of simplicity. This is not of much importance, as the most interesting helices are those described on surfaces of revolution. These may very conveniently be dealt with by the method given above.

#### IV. A Potential Problem. By D. N. Mallik\*.

IF V is the potential of an ellipsoid and XYZ the component forces, then of course

$$X = +Ax &c.$$
, and  $V = \int Ax dx + ...$ 

At an internal point, A B C are constants and then

$$V = V_0 + \frac{1}{2} (Ax^2 + By^2 + Cz^2).$$

(Minchin's Statics, vol. ii. p. 326.)

The same method is also applicable for an external point, although I have not seen it given in the text-books.

<sup>\*</sup> Communicated by Prof. A. W. Porter.

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In this case

$$\mathbf{A} = -2\pi\rho abc \int_{\mu}^{\infty} \frac{d\mathbf{\psi}}{(a^2 + \mathbf{\psi})^{\frac{3}{2}} (b^2 + \mathbf{\psi})^{\frac{1}{2}} (c^2 + \mathbf{\psi})^{\frac{1}{2}}},$$

where

$$\frac{x^2}{a^2 + \mu} + \frac{y^2}{b^2 + \mu} + \frac{z^2}{c^2 + \mu} = 1;$$

$$\therefore V = -2\pi\rho \ abc \left[ \int_0^x \int_\mu^\infty \frac{d\psi}{Q(a^2 + \psi)} x \, dx + \dots \right]$$

where

$$Q \equiv \sqrt{(a^2 + \boldsymbol{\psi})(b^2 + \boldsymbol{\psi})(c^2 + \boldsymbol{\psi})}.$$

We have now to change the order of integration. For this, let

$$\frac{x^2}{a^2 + \mu} + \frac{y^2}{b^2 + \mu} + \frac{z^2}{c^2 + \mu} = 1$$

be a curve in x and  $\mu$ ,  $\mu$  being the abscissa (y and z being

regarded as constants).

Then the integral depending on x extends evidently over the region included between this curve and a line parallel to the  $\mu$ -axis, i. e. from  $\mu$  given by

$$\frac{x^2}{a^2 + \mu} + \frac{y^2}{b^2 + \mu} + \frac{z^2}{c^2 + \mu} = 1 \text{ to } \mu = \infty,$$

and from  $x = x_1$  to x = x where

$$\frac{x_1^2}{a^2 + \mu} + \frac{y_1^2}{b^2 + \mu} + \frac{z_1^2}{c^2 + \mu} = 1$$

(with corresponding values of y and z).

$$\therefore \int Ax \, dx = -2\pi\rho \, abc \int_{\mu}^{\infty} \frac{d\psi}{Q(a^2 + \psi)} \int_{x_1}^{x} x \, dx$$

$$= -\pi\rho \, abc \int_{\mu}^{\infty} \frac{d\psi}{Q} \left( \frac{x^2}{a^2 + \psi} - \frac{{x_1}^2}{a^2 + \mu} \right)$$

$$\therefore V = -\pi\rho \, abc \int_{\mu}^{\infty} \frac{d\psi}{Q} \left( \frac{x^2}{a^2 + \psi} + \frac{y^2}{(b^2 + \psi)} + \frac{z^2}{c^2 + \psi} - 1 \right),$$
since
$$\frac{x_1^2}{a^2 + \mu} + \frac{y_1^2}{b^2 + \mu} + \frac{z_1^2}{c^2 + \mu} = 1.$$

Patna College, Bankipore. 6th June, 1907.

V. Experimental Determination of Magnetic Induction in an Elongated Spheroid. By Prof. D. N. Mallik\*.

1. In a paper on the magnetic induction in a spheroid due to a coil carrying current (Phil. Mag. Oct. 1907), I proved that if M be the induction at any point of such a spheroid,

M =  $\frac{pe}{a^2} (1 + 4\pi k) 2\pi mi \left[ 1 + \frac{2e^2c\log\left(1 + \frac{\lambda}{c}\right)}{3\pi\lambda\left(1 + \frac{a^2}{c^2}\right)} - \frac{2}{\pi} \right]$ = Ap, say,

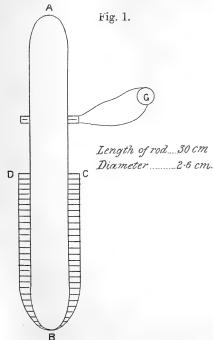
: if B = total magnetic induction over the semi-ellipsoid,  $B = \int M dS = A \int p dS = A a^2 \int dx$ ,

 $= (1 + 4\pi k) 2\pi mi \left(1 - \frac{4}{3\pi}\right) \int dx, \text{ nearly,}$ 

where dS is an element of surface, and dx an element of the major axis;

i. e.  $\frac{d\mathbf{B}}{dx} = \text{const.}$ 

In this form it is suitable for experimental verification, and I have made a series of experiments to test its accuracy.

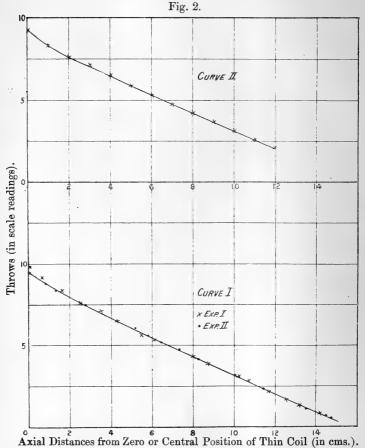


2. For this purpose, a rod AB (fig. 1) was prepared \* Communicated by the Author.

approximately spheroidal in form of very mild Bessemer steel well annealed, and the coil DC was wound round a thin wooden cap which just fitted it to half its length.

A current, the constancy of which was indicated by an ammeter, being passed through the coil, the soft steel rod was magnetized, and the object of the experiments was to explore the magnetic induction over the projecting portion of the rod.

3. In order to do this, a thin coil 4 inch in thickness having 36 turns (six turns, six deep), in series with a ballistic galvanometer, was slipped over the rod and placed at different positions beginning with middle of rod (the zero position), and corresponding throws on the reversal of current were noted. In the preliminary experiments (I. and II.) the thin coil was placed at random at different positions which were read



off by means of a telescope. The results are represented by Curve I., fig. 2, in which abscissæ represent distances from

the zero position, and ordinates the throws obtained at

corresponding positions.

4. In the final experiments the thin coil was moved up, a centimetre at a time, by means of a mechanical arrangement allowing of the actual displacement being read off on a vertical scale parallel to the axis of the rod. The following table gives the results obtained after a slight correction on account of the direct action of the magnetizing coil.

Distance from zero.	4×throw. Exp. III.	4×throw. Exp. IV.	Mean throw.	Throw per cm. of roo
0	37.6	36.7	9.29	
1	34.95	33.55	8.56	•73
2	32.2	31.05	7.9	.66
3	29:35	28.4	7.22	.68
4	26.6	26.1	6.59	•63
5	24.1	23.7	5.97	.62
. 6	21.4	21.35	5.34	.63
7	19.4	19.25	4.83	.51
8	17.12	17.16	4.28	.55
9	15.1	14.8	3.73	.55
10	13	12.8	3.22	•51
11	10.73	10.63	2.67	.55
12	8.9	8.6	2.19	.48

[In Exp. III. the exploring coil was moved from the zero position, and in Exp. IV. to the zero position.]

The results are also plotted in the Curve II. It will be seen that both sets of experiments give practically identical results, viz., that the curve is straight with a slight upward trend for the first three cms. from the zero. In order to explain this, we note that the rod is not altogether spheroidal in form, but is practically a cylinder with a rounded off end, so that the small coil for the first few centimetres from the zero position embraces more lines of force than if the rod were accurately spheroidal. We conclude therefore that the formula (§ 1) is experimentally verified for an elongated spheroid. It will therefore be necessarily also true of a cylindrical rod with rounded off ends, if the rod is sufficiently thin.

5. Further it is seen that in the latter case the lines of force are *radial* and uniformly distributed.

Moreover, if m be the total amount of induced magnetism over such a cylinder,

$$4\pi m = B$$
,

and  $\rho = \text{linear density of this magnetism}$ ,

$$4\pi \int \rho dx = B$$
,  
 $\frac{dB}{dx} = \rho = \text{const.}$ ;

or

or linear density of induced magnetism in a long thin cylinder due to a coil embracing half its length is constant.

6. The formula being thus experimentally verified, it may obviously be used to find how the value of k corresponding

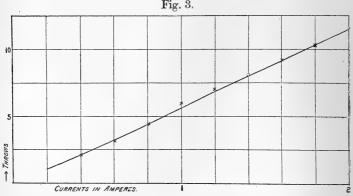
to different values of current, varies.

C

For this the small coil was placed in the central position and the throws of the galvanometer for different values of the current were noted. The following table gives the results of experiment.

Current in amperes.	Throw.
$\cdot 2$	1.05
•4	2.1
•6	3.15
•8	$4\cdot 4$
1	6
$1\cdot 2$	7.04
1.4	8.07
1.6	$9 \cdot 2$
1.8	10.02
2	11.55

These throws are plotted on a curve (fig. 3) in which these



are abscissæ and the currents are ordinates. We see that up to current of  $\cdot 8$  ampere k is absolutely constant, and then begins to vary slightly with the current, the variation being at first inappreciable. Unfortunately, however, the effect of the current in heating the coil as well as the rod was so great when the current was over 2 amperes, that it was not thought desirable to proceed with the experiments for stronger currents without considerable modification in the apparatus.

I have to thank Prof. Trouton for permission to work at the University College Laboratory for the purposes of the above investigation. VI. On Spherical Radiation and Vibrations in Conical Pipes. By E. H. Barton, D.Sc., F.R.S.E., Professor of Experimental Physics, University College, Nottingham\*.

IT is well known that the vibrations in parallel pipes may be treated by plane waves and elementary methods. When, however, a change is made from parallel to conical pipes the waves cease to be plane, and the method hitherto available is powerless to deal with the phenomena. Yet the importance of the subject is at least equal to that of parallel pipes, since the brass instruments in musical use are conical or quasi-conical, and also the oboe, bassoons, and English horn. Thus, apart from a knowledge of spherical radiation and its application to such pipes, the student is left without a clue to the phenomena occurring. He is accordingly somewhat at a loss to understand why a conical pipe, closed at the vertex and open at the base, should have the same pitch and the same complete series of harmonic tones as a parallel pipe open at both ends. Whereas, a parallel pipe if closed at one end falls in pitch about an octave and loses

all the evenly-numbered partials.

The mathematical aspect of the matter is of course treated with great generality and elegance in the classical treatises (see, for example, Rayleigh's 'Theory of Sound,' vol. ii. chaps. xi., xii., & xiv.). But the use in such treatises of the velocity potential as the dependent variable, slight as this obstacle is, may prove sufficient to prevent some readers from assimilating the articles in question. If, however, following Riemann, we take for the dependent variable the so-called condensation, which is a more familiar conception, the analysis is somewhat simplified and the whole problem is solved by methods within the range of every one familiar with the elements of the calculus. It seems desirable, therefore, that the physical student should be provided with a treatment intermediate between the recondite mathematical treatises on the one hand, and the mere statement of the musical facts respecting conical pipes on the other hand. This plan, already found useful in dealing with such students, is here given in the hope it may thus prove of service to others. Another matter which seems very puzzling, in the simple statement without proof, is the fact that in a conical pipe the anti-nodes remain in equidistant positions as for a parallel pipe, but that the nodes are all shifted, some considerably and others slightly.

\* Communicated by the Author.

<sup>†</sup> Partielle Differentialgleichungen und deren Anwendung auf physikalische Fragen. 1882. Sixth part.

This point is here illustrated graphically, the reason for the shifts which occur and their relative amounts being made

clear in a single diagram.

Fundamental Assumptions.—In attacking the problem of the spherical radiation of sound in air we simplify the analysis by making at the outset the following assumptions:—

(1) That the action of gravity is negligible.(2) That the effect of viscosity is negligible.

(3) That the motion is vibratory and devoid of rotation.(4) That the vibrations are small, so that writing the

density

 $\rho = \rho_0 (1+s)$ 

the "condensation" s is to be regarded as a small quantity often negligible in comparison with unity.

(5) That the velocities and accelerations of the air are small quantities whose squares and products are negligible.

It is easily seen that the above assumptions simply narrow down the discussion to the case in question, and do not

involve the loss of any generality we wish to retain.

In estimating the acceleration of the air two methods are open to us: (a) We may follow in thought an individual particle and note how much its velocity is increased per second; or: (b) We may fix attention on a spot in space and note how the speed changes of that particle (whichever it is) which is found there at the time in question. In other words, we may note the increase of speed of an individual in the procession, or the increase of speed of the procession as it passes a fixed point on the route. The relation between the two accelerations is given in hydrodynamical treatises. In our use of acceleration the first form should in strictness be taken, but, with the limitation (5), the distinction drops, as the difference is only of the second order of small quantities. Thus the second form, which is simpler, may always be used.

We have now to derive the differential equation for aerial vibrations in space of three dimensions, solve it and simplify to the case of spherical radiation, then apply the solution to

the various cases of conical pipes.

The differential equation is based upon (i.) the so-called equation of continuity, and (ii.) the equations of motion.

These we now take in the above order.

Equation of Continuity.—Consider an infinitesimal parallelepiped of edges dx, dy, and dz, and let the velocities of the air parallel to the axes of x, y, and z be denoted by u, v, and w respectively.

Then the mass of air entering the parallelepiped at the face dy dz in the time dt is  $\rho u (dy dz) dt$ , and that leaving by the opposite face in the same time is

$$\left\{\rho u + \frac{d(\rho u)}{dx} dx\right\} dy dz dt.$$

Hence, the mass lost by this pair of faces is

$$\frac{d(\rho u)}{dx} dx dy dz dt$$
.

Therefore, considering the other four faces in like manner, we have as the total mass lost by the parallelepiped in time dt the quantity

$$\left\{\frac{d(\rho u)}{dx} + \frac{d(\rho v)}{dy} + \frac{d(\rho w)}{dz}\right\} dx dy dz dt.$$

But this quantity can also be expressed in terms of the decrease of density, viz.:

$$-\frac{d\rho}{dt}\,dx\,dy\,dz\,dt.$$

Whence, equating the two forms, we have

$$\frac{d\rho}{dt} + \frac{d(\rho u)}{dx} + \frac{d(\rho v)}{dy} + \frac{d(\rho w)}{dz} = 0. \quad . \quad . \quad (1)$$

Now, since  $\rho = \rho_0(1+s)$ , the first term of (1) becomes  $\rho_0 ds/dt$ . Again,

$$\frac{d(\rho u)}{dx} = \rho_0 (1+s) \frac{du}{dx} + u \frac{d\rho}{dx} = \rho_0 \frac{du}{dx} \text{ nearly,}$$

the product of the two small quantities u and  $d\rho/dx$  being negligible. Thus for our case (1) becomes

$$\frac{ds}{dt} + \frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dr} = 0, \quad . \quad . \quad . \quad (2)$$

and this is the form of the equation of continuity for small

oscillations of a light elastic fluid.

Equations of Motion.—We have now to express, for the fluid in our parallelepiped, the condition that the product, mass into acceleration, equals the moving force to which it is subjected. The mass into acceleration is  $(\rho \, dx \, dy \, dz) \, du/dt$ . The moving force is the excess of that due to pressure, p,

behind over that due to pressure, p+dp, in front, or

$$p \, dy \, dz - \left(p + \frac{dp}{dx} dx\right) dy \, dz = -\frac{dp}{dx} dx \, dy \, dz.$$

Hence, equating, we find  $-dp/dx = \rho du/dt$ , or

$$\frac{1}{\rho} \frac{dp}{dx} = -\frac{du}{dt} \dots \dots (3)$$

But p is some function of  $\rho$ , and, whatever the form of the curve coordinating p and  $\rho$ , the small portion with which we are concerned may be considered straight. Hence, for our small vibrations, we can write

$$dp/d\rho = a^2$$
, some constant. . . . . (4)

We can easily see, by the method of dimensions, that a in (4) is of the nature of a velocity. For the left side of (4) is dimensionally

$$\frac{MLT^{-2}L^{-2}}{ML^{-3}} = L^{2}T^{-2} = (\text{velocity})^{2},$$

in which M, L, and T represent mass, length, and time respectively. From (4) we get

$$\frac{dp}{\rho} = \frac{a^2 d\rho}{\rho} = \frac{a^2 \rho_0 ds}{\rho_0 (1+s)} = a^2 ds \text{ nearly.}$$
 (5)

It should be noted here that we are not entitled to integrate (4) and draw from such result any conclusions about the general relation between p and  $\rho$ . On the contrary, the relation between them must be determined independently, and the general value of  $dp/d\rho = a^2$  derived from it.

Substituting (5) in (3), we obtain

Whence, for the other axes, we have by symmetry of notation

$$a^2 ds/dy = -dv/dt, \qquad (7)$$

and 
$$a^2 ds/dz = -dw/dt$$
. . . . . (8)

These three constitute the required equations of motion.

The Differential Equation.—We have now to derive from equations (2), (6), (7), and (8) the partial differential equation. We see that in addition to s, x, y, z, and t, the only variables we wish to retain, the above equations involve also u, v, and w. These last three must accordingly be

eliminated. On differentiating equation (2) with respect to time, we obtain

$$-\frac{d^2s}{dt^2} = \frac{d^2u}{dx\,dt} + \frac{d^2v}{dy\,dt} + \frac{d^2w}{dz\,dt}. \qquad (9)$$

Again, if we differentiate equation (6) to x, (7) to y, and (8) to z, and then add the results, we have

$$-a^{2}\left(\frac{d^{2}s}{dx^{2}} + \frac{d^{2}s}{dy^{2}} + \frac{d^{2}s}{dz^{2}}\right) = \frac{d^{2}u}{dt\,dx} + \frac{d^{2}v}{dt\,dy} + \frac{d^{2}w}{dt\,dz}. \quad (10)$$

But since  $d^2u/dx dt = d^2u/dt dx$ , because the order of partial differentiation is indifferent, the right sides of (9) and (10) are identical. Thus, equating their left sides, we have

$$\frac{d^2s}{dt^2} = a^2 \left( \frac{\overline{d^2s}}{dx^2} + \frac{d^2s}{dy^2} + \frac{d^2s}{dz^2} \right)$$
or
$$\frac{d^2s}{dt^2} = a^2 \nabla^2 s, \qquad (11)$$

where for brevity's sake  $\nabla^2$  denotes  $\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$ .

This is the general form of the differential equation applicable to small vibratory disturbances of a light compressible medium in space of three dimensions.

Plane Waves.—As a check upon this result, let us reduce it to the case of plane waves in the plane of yz, and proceeding therefore in the direction x. Thus s is a function of t and x only and is independent of y and z. Hence  $\nabla^2 s = d^2 s / dx^2$  and (11) becomes

$$\frac{d^2s}{dt^2} = a^2 \frac{d^2s}{dx^2}, \qquad (12)$$

which is the well-known form of equation for plane waves. To examine if a has the right value here let the specific volume be U, then  $\rho = 1/U$  and  $d\rho = -dU/U^2$ .

$$\therefore a^2 = \frac{dp}{d\rho} = \left(\frac{-dp}{dU/U}\right) U = EU = E/\rho = \gamma p/\rho, \quad (13)$$

in which E denotes the volume elasticity and  $\gamma$  the ratio of the two specific heats. Thus, the ordinary value is seen to hold.

Solution for Spherical Waves.—Let us now transform to polar coordinates defined by

$$x = r \sin \theta \cos \phi$$
,  $y = r \sin \theta \sin \phi$ , and  $z = r \cos \theta$ . (14)

Then it is shown in text-books on the calculus (e. g. Williamson's 'Differential Calculus') that

$$\nabla^2 s = \frac{d^2 s}{dr^2} + \frac{2}{r} \frac{ds}{dr} + \frac{1}{r^2 \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{ds}{d\theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{d^2 s}{d\phi^2}.$$
 (15)

Now suppose we have symmetry about the centre of the system, so that s is a function of r only. Then  $ds/d\theta = 0$  and  $ds/d\phi = 0$ . Hence, for this case, (15) reduces to

$$\nabla^2 s = \frac{d^2 s}{dr^2} + \frac{2}{r} \frac{ds}{dr} = \frac{1}{r} \frac{d^2(rs)}{dr^2}.$$
 (16)

Equation (11) accordingly becomes

$$a^{2} \frac{d^{2}(rs)}{dr^{2}} = \frac{d^{2}(rs)}{dt^{2}}. (17)$$

The general solution of this may be written

$$rs = f_1(r-at) + f_2(r+at)$$
, . . . (18)

where  $f_1$  and  $f_2$  denote arbitrary functions. This solution obviously consists of both diverging and converging waves of spherical form, of any periodic or non-periodic type and travelling with radial speed a. For diverging waves of simple harmonic type (18) becomes

$$s = \frac{c}{r}\cos k(r - at). \quad . \quad . \quad . \quad (19)$$

To denote the speed u of the air along the radius r, we derive from (6) and (19)

$$\frac{-du}{dt} = a^2 \frac{ds}{dr} = \frac{a^2 c}{r} \left\{ -k \sin k(r - at) - \frac{1}{r} \cos k(r - at) \right\}. \quad (20)$$

Thus

$$u = -a^2 \int \frac{ds}{dr} dt = \frac{ca}{r} \left\{ \cos k(r - at) - \frac{1}{kr} \sin k(r - at) \right\}. \quad (21)$$

Again, if displacements along r be denoted by  $\xi$ , we have by another integration

$$\xi = \int u dt, \quad \text{or}$$

$$\xi = -\frac{c}{kr} \left\{ \sin k(r - at) + \frac{1}{kr} \cos k(r - at) \right\}. \quad (22)$$

We may thus see, from equations (19), (21), and (22), that it is only the condensation s whose change of phase is restricted to the ordinary one inseparably associated with the

advance of a progressive wave. Its amplitude, however, suffers diminution by varying inversely as r. But, owing to this diminution or attenuation with advance, we have in the other equations the factors 1/r and also  $1/r^2$ , one applying to a sine and the other to a cosine function. Hence the speed u and the displacement  $\xi$  each exhibit, during advance, an additional slight change of phase (as the sine and cosine terms are differently diminished), beyond that always present in a progressive wave. But, where r is great enough to make 1/kr negligibly small, (21) and (22) become approximately

$$u = \frac{ca}{r} \cos k(r - at), \quad . \quad . \quad . \quad (23)$$

and 
$$\xi = \frac{-c}{kr} \sin k(r - at). \qquad (24)$$

Reflexion at Pole.—Let us now regard the two spherical waves of (18) as a converging one and a diverging one to which the other gives rise by reflexion at the pole or centre of the system. And let it be required to determine the relation between  $f_1$  and  $f_2$  so resulting. The total current across the surface of a sphere of radius r is  $4\pi r^2 u$  and, for r=0, must vanish, since all is symmetrical about the pole or origin of coordinates. That is, u cannot be infinite and so make  $r^2 u$  finite for r=0. But, if  $4\pi r^2 u$  vanishes at r=0 for all values of t, so also will  $4\pi r^2 du/dt$  vanish. And this condition is easier to fulfil analytically. Thus from (6) and (18) we have

$$4\pi r^2 du/dt = -4\pi a^2 r^2 ds/dr$$

$$= 4\pi a^2 \{f_1(r-at) + f_2(r+at)\} - 4\pi a^2 r \{f_1'(r-at) + f_2'(r+at)\},\,$$

where f' denotes the first derived function of f.

Hence, putting du/dt=0 for r=0, we find

$$0 = f_1(-at) + f_2(at)$$
 . . . (25)

as the relation between  $f_1$  and  $f_2$ . But we see from (18) that the right side of (25) is the value of (rs) for r=0. Hence, we may write as the condition at the pole

$$rs = 0$$
 for  $r = 0, \dots (26)$ 

or, rs must vanish with r.

Thus, at the pole, a condensation is reflected as a *rare-faction* and *vice versa*, somewhat as in the case of reflexion at the *open* end of a parallel pipe.

Conical Pipes.—To apply equation (17) to conical pipes

we must choose a form of solution corresponding to stationary waves. Thus, let rs be everywhere proportional to  $\cos kat$ . Then  $d^2(rs)/dt^2 = -k^2a^2(rs)$ , and equation (17) transforms into

$$\frac{d^2(rs)}{dr^2} + k^2(rs) = 0. . . (27)$$

The general solution of this may be written

$$rs = (A\cos kr + B\sin kr)\cos kat, \quad . \quad . \quad (28)$$

where A and B are arbitrary constants. These are to be determined for each case by the position and nature of the ends of the pipe. There are accordingly a number of

separate cases to consider.

Open Ends.—First let both ends of the conical pipe be open. Then obviously the condition at the end is approximately s=0. For, at the ideal open end there can be neither condensation nor rarefaction. Let the coordinates of the ends of the pipe be  $r_1$  and  $r_2$ , measured from the vertex of the cone if completed. Then, we have from (28) for the terminal conditions,

A  $\cos kr_1 + B \sin kr_1 = 0$  and A  $\cos kr_2 + B \sin kr_2 = 0$ ; whence, by the elimination of A/B, we obtain

$$\sin k(r_2-r_1)=0$$
 or  $k(r_2-r_1)=n\pi$ .

This may be written

$$r_2 - r_1 = n\lambda_n/2$$
 or  $N_n = \frac{na}{2(r_2 - r_1)}$ , . . (29)

where n is an integer; for since s is proportional to  $\cos kat$ ,  $k=2\pi N/a=2\pi/\lambda$ , N being the frequency and  $\lambda$  the wavelength of the motion. Thus, for a conical pipe with open ends, the pitch of the prime tone and the form of the series of other natural tones are like those for an open-ended parallel pipe. This might nave been anticipated from the similarity of the differential equations and the conditions for the open ends in each case, There is, however, this slight difference that  $r_2-r_1$  is the slant length of the conical pipe and not its axial length. As to the segments into which the pipe is divided when emitting its higher natural tones, it follows from equation (29) that the antinodes are equidistant. When dealing with the next case, it will be seen that this simplicity does not extend to the nodes.

Closed Ends.—The condition at closed ends is obviously u=0; consequently du/dt=0 there also. But by equation (6)  $du/dt=a^2ds/dr$ , if u denotes the velocity along r. We may thus write as our condition for a closed end ds/dr=0.

Applying this to equation (28), we find, after a little transformation,

$$A(\cos kr_1 + kr_1 \sin kr_1) = B(kr_1 \cos kr_1 - \sin kr_1),$$

and 
$$A(\cos kr_2 + kr_2 \sin kr_2) = B(kr_2 \cos kr_2 - \sin kr_2).$$

or

On dividing out by the cosines and writing  $\tan \theta_1$  for  $kr_1$  and  $\tan \theta_2$  for  $kr_2$ , we may eliminate A/B between the above equations. Thus

$$A/B = \frac{\tan \theta_1 - \tan kr_1}{1 + \tan \theta_1 \tan kr_1} = \tan (\theta_1 - kr_1) = \tan (\theta_2 - kr_2),$$
$$kr_2 - \tan^{-1} kr_2 = kr_1 - \tan^{-1} kr_1. \qquad (30)$$

The transcendental form of this equation shows that the nodes are not equidistant in a conical pipe. We will presently find where they are in the important case of a complete cone with open end.

Closed Cone.—To treat the case of a cone continued to the vertex and with base closed, we have simply to write  $r_1=0$  in equation (30) and R as the slant length of the cone for  $r_2$ . This gives

$$\tan k \mathbf{R} = k \mathbf{R}$$
. . . . . . (31)

To solve this equation, which we may regard as  $\tan x = x$ , we may proceed graphically. Thus plot the two graphs y = x and  $y = \tan x$ . Then their intersections will give the roots required. See fig. 1, p. 80 as an illustration of this. The equation may also be solved by successive approximations by which (in another connexion) Lord Rayleigh finds ('Theory of Sound,' vol. i. p. 334),

$$\begin{bmatrix}
R \\
= x/\pi = 0, & 1.4303, & 2.4590, & 3.4709, & 4.4747, & 5.4818, & 6.4844, & & \\
= \theta_1, & \theta_2, & \theta_3, & \theta_4, & \theta_5, & \theta_6, & \theta_7, & \text{say,}
\end{bmatrix} (32)$$

Thus these quantities, denoted by the  $\theta$ 's, each multiplied by  $\pi$ , give the first seven values of kR in equation (31).

Now since  $\theta_1 = 0$ , we may write  $(k_n R) = \pi \theta_{n+1}$ . But we also have as the general relation  $k_n = 2\pi N_n/a$ . Hence, we may write for the frequency of the *n*th tone natural to the closed cone

$$N_n = \frac{a}{2R} \theta_{n+1} \dots$$
 (33)

Thus the frequencies are directly proportional to the speed of sound, inversely proportional to the slant length of the cone and the relation of the various possible tones in the series is defined by equation (32) giving the roots of (31). Open Cone.—We now consider the case of a complete cone with base open. At the open base, we have, as before for an open end, the condition rs=0. And at the vertex, the origin of coordinates, we have from equation (26) that rs=0 there also. So that although one end is open and the other closed, we have the apparent anomaly that the same condition applies to each. Hence if R is the coordinate of the base, i. e. R is the slant length of the cone, we have from (29)

 $R = m\lambda_m/2$  or  $N_m = m\alpha/2R$ , . . . (34)

where  $N_m$  is the frequency of the mth natural tone and  $\lambda_m$  its wave-length, a being the speed of sound. This then shows, what has before been remarked upon as strange, that a cone open at the base and closed at the vertex gives practically the same fundamental and the same full harmonic series of other natural tones as are obtainable from a parallel pipe of the same length and open at both ends. Of course, when the corrections for open ends are taken into account, the statement as to pitch and length suffers a slight modification. For the double open-ended parallel pipe has two ends needing correction and the cone only one; moreover their diameters may differ. But if a cone and an open-ended parallel pipe are prepared of slightly different lengths so that their fundamentals are in unison, then their other partials will be in accord also. This may easily be verified by pipes of zinc tested with a set of tuning-forks forming the harmonic series of relative frequencies 1, 2, 3, 4, &c.

We see from the first form of (34) that the wave-length is inversely as the order of the tone produced; hence the antinodes are all equidistant. This, however, does not apply to the nodes. To determine the positions of the nodes we must refer to equations (31) to (34). Now equation (33) gives in terms of  $\theta$  the various values of N for a closed cone of fixed slant length R. Let us, however, substitute the variable r for the constant R and, dropping the subscript

of N, rewrite this equation as follows:—

$$2Nr/a = \theta_1, \ \theta_2, \ \theta_3, \ \theta_4, \ \theta_5, \ \theta_6, \ \text{or} \ \theta_7, \&c.$$
 (35)

We may now regard both N and r as variables which must satisfy (35), r being the slant length of a closed cone. Again, equation (34) gives the frequencies of the various tones natural to the open cone. Let us rewrite it, dropping from N its subscript and writing for m on the right side the series of natural numbers which it represents. We thus obtain

$$2NR/a=1$$
, 2, 3, 4, 5, 6, or 7, &c. . . (36)

Here we consider the slant length R of our open cone as a constant and N to vary in accordance with the numbers on the right side of the equation. Now, on dividing equation (35) by (36) we eliminate the frequency N and obtain the required relations between r and R, viz.:—

$$\frac{r}{R} = \frac{\theta_{1}}{1}, \quad \frac{\theta_{1} \text{ or } \theta_{2}}{2}, \quad \frac{\theta_{1}, \theta_{2} \text{ or } \theta_{3}}{3}, \quad \frac{\theta_{1}, \theta_{2}, \theta_{3} \text{ or } \theta_{4}}{4}, \quad \frac{\theta_{1}, \theta_{2}, \theta_{3}, \theta_{4} \text{ or } \theta_{5}}{5}, \\
\frac{\theta_{1}, \theta_{2}, \theta_{3}, \theta_{4}, \theta_{5} \text{ or } \theta_{6}}{6}, \quad \text{or } \frac{\theta_{1}, \theta_{2}, \theta_{3}, \theta_{4}, \theta_{5}, \theta_{6} \text{ or } \theta_{7}}{7}, &c.$$
(37)

It is necessary to cross combine the right sides of (35) and (36) in this way to obtain all the values sought. The denominator of any one of the fractions on the right of (37) shows the order of the tone being emitted by the pipe. The various values of r/R obtained by taking the various  $\theta$ 's in the numerator of that fraction locate the nodes for the tone in question. The series of  $\theta$ 's in each numerator is finite, being limited by the obvious fact that r/R cannot exceed unity. The first few nodal positions are given in Table I. They are also exhibited graphically together with the positions of the

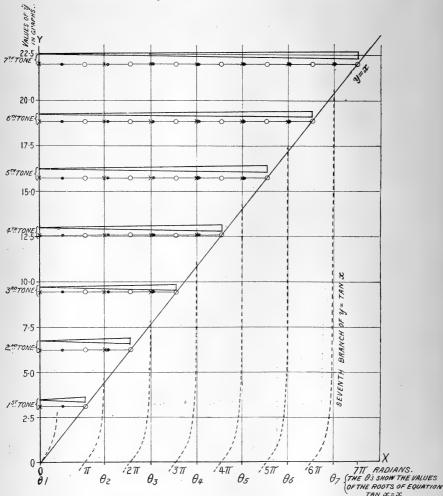
TABLE I.—Nodal Positions of an Open Cone.

Order m of Natural Tone; i. e. denominator of fraction on right side of equation (37).	Nodal Positions; $i.\ e.,\ values\ of\ r/\mathbf{R} = \theta/m\ in\ equation\ (37).$						
1	0	1					
2	0	0.7152			ļ		
3	0	0.4768	0.8197				
4	0	0.3576	0.6148	0.8677			
5	0	0.2861	0.4918	0.6942	0.8949		
6	0	0.2384	0.4098	0.5785	0.7458	0.9136	
7	0	0.2043	0.3513	0.4958	0.6392	0.7831	0.9263
Values of $\theta$ 's in numerators of fractions on right side of equation (37)	$\left.\begin{array}{c} \theta_1 \\ 0 \end{array}\right.$	θ <sub>2</sub> 1·4303	$\theta_{3}$ 2.4590	$\theta_4 \\ 3.4709$	$\theta_5 \\ 4.4747$	$ heta_6$ 5:4818	$\begin{array}{c c} \theta_7 \\ 6.4844 \end{array}$

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antidodes in fig. 1. In this diagram the graph y=x is shown by a full line and the branches of  $y = \tan x$  by broken lines. The abscissæ of their intersections show the values of the roots of the equation,  $\tan x = x$ .

Fig. 1.—Vibrating Segments of an Open Cone. The circles show the equidistant antinodes and the crosses show the nodes located by the intersections of x=y and  $y=\tan x$ .



To show the segments of one pipe of fixed length when emitting its various tones, a number of such diagrams would be needed. To avoid this repetition, a series of pipes is shown in the upper part of the diagram. These are of various length so that the longest at the top is shown with the segments corresponding to its seventh natural tone. Passing down the series, we reach the last pipe, the shortest of all, with one segment only as when emitting its fundamental. The antinodes are indicated by small circles and the nodes by crosses. The equidistant positions midway between the antinodes are shown by dots.

Experiments by Mr. D. J. Blaikley have shown the existence of these nodes in positions slightly displaced from equidistances, each node being moved towards the vertex from the corresponding equidistant position. Further, it was found by Blaikley that the displacement was the greater for those nodes which are nearer the vertex. Or, in other words, "the nodes in the cone are at increasing distances apart, reckoning from the open end, and at the apex of the cone is a node common to all the notes." These nodal positions were established by Blaikley with an experimental bugle made in sections. On taking this to pieces, thin metal diaphragms were inserted at the positions of the nodes for a certain note, and their presence was found not to prevent the production of the note in question. The diaphragms had each a few small holes to admit the passage of the player's breath, but prevented all free vibration at the place.

University College, Nottingham, June 7, 1907.

VII. On the Rupture of Materials under Combined Stress:—
Tension and Hydrostatic Pressure. By W. Ellis Williams, B.Sc., Research Fellow of the University of Wales\*.

THE connexion between the rupture of a solid body and the stress causing it is at present but vaguely understood, and a number of different theories have been put forward to enable the tendency to rupture to be calculated from the stresses acting on the body by the methods of elastic theory. The principal of these are †:—

- (1) Lamé.—Rupture occurs when the greatest tension has reached a certain limit.
- (2) Poncelet and St. Venant.—Rupture occurs when the greatest extension has reached a certain limit.

<sup>\*</sup> Communicated by Prof. E. Taylor Jones. † Love, 'Elasticity,' vol. i. p. 106.

(3) Tresca.—Rupture occurs when the difference between the greatest and least principal stresses exceeds a certain limit.

(4) COULOMB.—Rupture occurs when the greatest shear

has reached a certain value.

The theory which has been most widely adopted is that attributed to Poncelet, which agrees closely with experimental results for a few substances, notably for cast iron. In this theory the extension is to be calculated from the applied stresses by means of the ordinary elastic constants, and the theory requires for each body only one other constant,

the limiting extension.

Some years ago Voigt \* made a series of experiments on the effect of hydrostatic pressure on the breaking strength or rocksalt and of wax, and obtained results in direct opposition to Poncelet's theory. Voigt measured the breaking-stress of rocksalt specimens enclosed in a cylinder containing carbonic acid gas under a pressure of 50 atmospheres, and found that the tension necessary to break the specimen was the same as when the experiment was performed under atmospheric pressure, while according to Poncelet's theory it should be twice as great. Voigt concludes from his experiments that the third theory due to Tresca is the most satisfactory. The results could, however, be equally well explained by Coulomb's theory, as both give nearly the same result for this kind of stress combination. The following experiments were carried out to confirm and extend Voigt's results, and especially to repeat them under the highest possible hydrostatic pressure. The range of pressure obtained in the present experiments is 900 atmospheres or 9 kg. per sq. mm., which is twenty times the breaking-stress of rocksalt, the material experimented upon.

#### Description of Apparatus.

The hydrostatic pressure was obtained by means of a Schaffner and Budenberg screw-pump furnished with a Bourdon gauge, reading to 1500 atms.

The specimens were tested in a steel cylinder of the following dimensions:—Inner diameter 4 cms., outer diameter

10 cms., length 80 cms.

The cylinder was fixed vertically in an iron stand built into the stone floor of the room, so as to avoid all shocks and vibrations which might tend to break the test-pieces. The specimens were ruptured by means of the electromagnetic

<sup>\*</sup> Voigt, Annalen der Physik, lvii. p. 452 (1899).

pull on an iron rod placed partly inside a coil carrying an electric current. The actual arrangement of the apparatus

Fig. 1. 

is shown in the accompanying figure. In order that the force might be as great as possible two coils were used, wound on the same brass tube and about 15 cms. apart. This tube served also to guide the iron cores, which were connected together so that they moved as one rigid piece, the distance between them being the same as that between the coils. In order to diminish the friction between the cores and the guidingtube, a small frame carrying three rollers was fixed to each core. In the part of the brass tube above the upper coil a long slit was cut reaching to within 2 cms. of the top of the coil. A piece of thick steel wire was soldered to the upper end of the iron core and bent so as to travel in this slit, it thus prevented the iron core from turning, and at the same time served as a hook by which the core could be hung from the piece to be tested. The other end of the testpiece was supported on a ring-nut travelling on the brass tube on which a corresponding screw was cut. By adjusting this ring the core could always be suspended in the same position in the tube although the test-pieces might vary in length. In order to show when the test-piece was broken, it was arranged that the iron core in falling should break the electric circuit.

For this purpose a ring carrying a small ebonite mercury cup connected by a piece of flexible wire to the upper coil was made to slide on the tube below the hook mentioned above. A wire coming from the cylinder cover dipped into this cup and closed the electric circuit of the two coils. When the test-piece was broken the steel hook in falling carried the ring with it and so broke the connexion. In the experiments the current was gradually increased until the connexion was broken and the maximum

reading of the amperemeter noted.

The connexion between the force exerted by the iron cores and the current in the coils was measured in a preliminary experiment. The brass tube carrying the coils was placed in the

cylinder in the position which it occupied in the breaking

tests. The cylinder being left open, the iron core was hung from one pan of a balance placed directly above the cylinder, and the force for each current measured by placing weights in the other pan. The values obtained are given in the following table:—

Current in amps.	Force in grammes.	Friction in grammes.	Current.	Force.	Friction.
0 4·3 5·53 6·7 8·16 9·03	553 870 1042 1282 1670 1905	2 2 3 5 5 5 5	11·2 13·0 14·8 15·7 16·0	2470 3120 3570 3700 3920	5 10 20 20 20 20

It will be seen that the maximum force obtained was nearly 4 kilos, and that the friction never exceeded 1 percent. of the total force.

## Preparation of the Rocksalt Pieces.

Owing to the extreme brittleness of the rocksalt it was found necessary to suspend the pieces in such a way that there should be no bending moment on the piece, that is to say the line of resultant stress must pass through the centre of each cross section of the rocksalt rod. For this purpose the apparatus shown in fig. 2 was made. It consists of two

Fig. 2.

cylindrical pieces made in aluminium, with holes of the proper size into which the rocksalt rods could be fastened with wax. Each piece has a short steel rod pointed at each end screwed in. The inner two of these points serve to suspend the piece in the testing apparatus, while the other two serve to mount the piece in the lathe during the preparation of the rocksalt rod. These steel rods were carefully fitted in on the lathe so that they were exactly parallel to the axes of the cylindrical pieces. The rocksalt was first split with a knife into prisms about 3 cms. long, and was then worked approximately cylindrical with a fine file.

The aluminium end-pieces were then fixed on, and while the wax was still soft the whole was pushed into a brass tube into which they accurately

fitted, and left in until the wax hardened. This ensured that the axes of the two end-pieces should be in the same straight line, and consequently the axes of the four steel points also

lay in this line.

The whole was then placed on a watchmaker's pair of turns, and by means of a pulley on one of the pieces the rocksalt was turned with a file and then polished with a piece of moist wood. The pieces were turned down a little thinner in the middle as shown in the figure, the diameter of the thinnest part being about 2 or 3 mms. This process of preparing the rocksalt ensured that the two points from which it was suspended were exactly in the same straight line with the axis of the rod.

As the fluid used in the pump and cylinder was water, it was necessary to protect the rocksalt from its action. For this purpose a small brass tube was screwed on the lower of the two aluminium pieces, and the vessel thus formed was filled with nitrobenzol, which completely covered the rocksalt. It was previously ascertained that this fluid had no dissolving power for rocksalt and did not affect its breaking strength.

#### RESULTS.

It was found from the beginning that the value of the breaking tension varied very much for different specimens. At first it was thought that this variation was due to imperfections in the apparatus and methods of preparation of the rocksalt rods. All improvements in the apparatus did not, however, alter the results, and the conclusion was finally come to that the differences were due to variations occurring in the rocksalt itself.

Two different crystals were used in the experiments—one about  $6 \times 4 \times 2$  cms., and the other a large square block about

10 cms. each way.

The first piece was all used up in preliminary experiments in determining the breaking stress of rocksalt with weights, and the results obtained were much better than the results afterwards obtained in exactly the same way with rods cut from the larger block. It has been shown by Voigt that the breaking stress of crystal specimens depends on the direction in which they are cut relative to the crystalline axes, and that in rocksalt this variation is very marked. I found that in specimens from the large block cut in a direction making an angle of 45° with the crystalline axes, the breaking stress was 4000 grammes per sq. mm., or more than four times the maximum result with pieces cut parallel to the axes. It is possible therefore that the variations observed are due to small irregularities in the crystalline structure of the pieces

which cause the direction of the axes to vary from point to point of the crystal. Although owing to these variations it was impossible to make any exact comparison between the breaking strength with and without external pressure, yet as the hydrostatic pressure employed was many times greater than the breaking stress of rocksalt, the results show clearly that the phenomena are not in accordance with Poncelet's theory. Thus the strength of rocksalt under atmospheric pressure varied from 400 to 900 grammes per sq. mm. with a mean of 600 grammes. According to Poncelet's theory the strength under 1000 atmospheres should be 10,000 grammes, while the values actually obtained range between 500 and 1000 grammes.

The actual results obtained are shown in the following

table:—

## Tests without external pressure.

Specimens from first block, broken with weights:-

449, 372, 390, 391, 497, 466, 530, 510, 407, **364**, 485, grms./sq. mm.

Mean:—447 grms./sq. mm.

Specimens from second block of salt, broken with weights:—503, 600, 901, 940, 570, 381, grms./sq. mm.

Mean:—649 grms./sq. mm.

Specimens from second block, broken in the cylinder with electromagnetic apparatus, but without pressure:—

630, 700, 700, 400, 720, 380, 300, 427, grms./sq. mm. Mean:—537 grms./sq. mm.

## Tests under pressure.

### All specimens from second block.

Pressure.	Breaking Stress.		
150 atms.	932 grms./sq. mm.		
200 ,,	502 ,,		
500 ,,	501 ,,		
960 ,,	800 ,,		
965 "	840 ,,		
970 ,,	540 ,,		
900 ,,	587		
980 ,,	853 ,,		

Two specimens were not broken with highest current employed, giving strength greater than

820, 762 grms./sq. mm. respectively.

The five specimens tested at a pressure from 900-1000 atms. give a mean of 724 grms/sq. mm.

# Experiments on Aluminium Wires.

It was thought desirable to extend the experiments to ductile materials, which might possibly behave in a different manner to a brittle substance like rocksat. Lead and tin were first tried, but it was found difficult to obtain satisfactory results owing to the fact that rupture takes place gradually, and the result depends on the time during which the stress is applied. Finally, aluminium was chosen as having a comparatively low breaking strength, and giving consistent results when tested with weights. A length of hard-drawn aluminium wire, 48 mm. diameter, was cut into pieces a few centimetres long, and alternate lengths tested with and without pressure. The results were:—

Breaking stress without external pressure.

13.6, 13.8, 13.6, 14.0, 13.2, kilos/sq. mm. Mean:—13.6 kilos/sq. mm.

Breaking stress under 700 atms. pressure.

14·2, 14·2, 12·7, 12·8, 15·2 kilos/sq. mm. Mean:—13·8 kilos./sq. mm.

There is thus no appreciable difference in the breaking stress with and without external pressure.

The above experiments were carried out in the Physical Laboratory of the University of Munich, and my best thanks are due to Professor Röntgen for his help in carrying out the work, and especially for suggesting the methods employed to overcome the difficulties connected with the preparation of the rocksalt pieces, and the electromagnetic apparatus for obtaining the breaking tension.

University College, Bangor, 1907.

VIII. On the Secondary Undulations of Oceanic Tides. (An Abstract.) By K. Honda, T. Terada, and D. Isitani, Tokio Imperial University, Japan\*.

#### [Plates I.-VI.]

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§ 1. Introduction.
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§ 7. Sea-Waves and Secondary Ondata § 8. Oscillations of Large Bays and Anomaly of Tides.

#### § 1. Introduction.

THE tidal curves obtained by self-recording tide-gauges are often accompanied by a peculiar zigzag or secondary undulation of considerable amplitude, which becomes perceptible at a station situated in a bay or an estuary. fact seems to have been noticed by many earlier observers.

Without discussing all these earlier contributions to the subject, we will briefly mention some comparatively recent valuable investigations. David Milne† discussed the remarkable undulations of July 1843 which were noticeable on the coasts of Great Britain, and ascribed their origin to the storm then prevailing in that district. Admiral Smyth! referred to the same phenomenon observed at Mazzara, where it has long been termed Mirabia or Marrobbio. Sir George Airy believes that the secondary undulation is the seiches between the Sicilian and African coasts. This phenomenon has also been observed on the coast of Italy and the northern

\* Communicated by the Authors.

+ D. Milne: "On a remarkable Oscillation of the Sea observed at various Coasts of Great Britain," Trans. Roy. Soc. Edinb. 1844.

† Smyth: Memoir descriptive of the Resources, Inhabitants, and

Hydrography of Sicily; London, 1824.

§ G. Airy: "On Tides in Malta," Phil. Trans. Roy. Soc. London, clxix. 1878.

|| G. Grablovitz: "Ricerche sulle maree d'Ischia," Rend. Acc. Lincei, vi. 1890. "Sulle osservazioni mareografiche in Italia e specialmente su quelle fatte ad Ischia," Atti del I. Congr. Ital., Genova, 1893. R. Sieger: "Niveauveranderungen an Skandinavischen Seen fund Küsten," Verh. Sten Deutsch. Geogr., Wien. E. Brückner: "Ueber Schwankungen der See und Meere," Verh. 9ten Deutsch. Geogr., Wien, 1892.

coasts of Europe. In 1895 W. Bell Dawson\* read a paper before the Royal Society of Canada, in which he demonstrated the existence of secondary undulations of considerable

amplitude.

Professor Duff† concluded, from observations at many stations along the coast of the Bay of Fundy and the Gulf of St. Lawrence, that the periods of the secondary undulation were peculiar to each station, and that the phenomenon here partook of the nature of seiches excited by the low barometric conditions. H. C. Russell t states that at Sydney the undulations are in most cases due to atmospheric disturbances. Napier Denison & of Toronto Observatory, made a systematic study of the subject in connexion with the barometric changes, and attributed the phenomenon to long waves generated by air waves of considerable wave-length, which accompanied the low barometric pressure. For several years Professor Giovanni Platania has been investigating the secondary undulations in the Gulf of Catania, as well as on other coasts of Italy, and has noticed that the oscillations of conspicuous amplitude occur in connexion with barometric disturbances.

In the bays of Japan on the Pacific coast, the phenomenon is sometimes so remarkable that it is commonly known as In the harbour of Nagasaki it is called Abiki; and here the amplitude of undulation frequently exceeds 60 cms. This yota or abiki is frequently observed during the calm weather which immediately precedes an approaching low

barometric pressure.

Professor F. Omori¶ studied the secondary undulations of Ayukawa, Misaki, and Hososhima mareograms in connexion with his discussion of the several destructive sea-waves, and found that the periods of the waves are the same as those observed in ordinary cases. The records \*\* taken from the tide-gauges at Indian coasts, of the waves which accompanied

\* Dawson: "Notes on Secondary Undulations," Proc. Roy. Soc. Canada, May 1895.

† Duff: "Seiches on the Bay of Fundy," Amer. Journ. Sci. iii. 1897. "Periodic Tides," 'Nature,' lix. 1899.

† Russell: "The Source of Periodic Waves," 'Nature,' lvii. 1898. § Denison: "Secondary Undulations of Tide-gauges," Proc. Can. Inst. i. 1898. "The Origin of Tidal Secondary Undulations," *ibid.* i. 1898. || Platania: "Le librazioni del mare con particolare riguardo al Golfo di Catania," Atti del V. Congr. Geogr. Ital., Napoli, 1904. "I fenomeni

in Mare durante il ferremoto di Galabria del 1905," 1907. "Nuove ricerche sulle librazioni del mare," 1907.

¶ Omori: Publications of Earthquake Investigation Committee, xxxiv. 1900.

\*\* Omori: Publications of Earth. Inves. Comm. lvi. 1906; Proc. Tokio Math.-Phys. Soc. ii. 1905.

the great eruption of Krakatoa 1888, were also found to show the same periods as were frequently found in ordinary cases. He explained this interesting fact by supposing that a bay, or a certain portion of the sea, makes some fluid pendulum motion with its own period. Professor H. Nagaoka\*, in his paper on the hydrodynamical investigations of sea-waves, expressed the desirability of a special inquiry looking towards an explanation of this phenomenon. The suggestion was taken up by the Earthquake Investigation Committee, with the result that the task of making a series of systematic observations was imposed upon us.

The observations were carried out during the years 1903 to 1906; the number of bays and coasts where work was done amounts to about sixty in all, extending from Hokkaido to Kiushiu. The work consisted *firstly* in finding the periods of the undulations peculiar to each bay or coast; and secondly in comparing the phases of the different portions of a bay by simultaneous observations—which latter, however, was accomplished only for a number of the most typical

bays.

In most cases portable, self-recording tide-gauges (Pl. I., figs. 1, 2) were used, the construction and theory of which has been already published in the Phil Mag. vol. x. p. 253 (1905).

#### § 2. General Conclusions.

The general conclusions †, which have been drawn from the thorough study of the numerous records obtained, are given in the following propositions. In discussing our results we have availed ourselves of the valuable records made by Lord Kelvin's tide-gauges at ten different stations. These instruments have been set up at various places on the coasts of the Pacific and of the Japan Sea, and some of them have been in working operation twenty years.

1. On the Pacific coasts, free from any inlet in the coastline, the secondary undulation is quite unnoticeable, and of a very irregular nature.

2. On the coasts of the Japan Sea the secondary undulation on the open coast is observable, though the periods

of the undulations are not regular.

\* Nagaoka, Proc. Tokio Math-Phys. Soc. i. 1903.

<sup>†</sup> In Pl. II, a map of Japan is given. The locations of the principal observation stations are marked by points.

- 3. In a bay of considerable area, or in a shallow bay with a narrow opening towards the ocean, the secondary undulation is in ordinary cases imperceptible.
- 4. In a deep bay or estuary, the breadth of which is not large in comparison with its length, the secondary undulations are most pronounced.
- 5. In bays or open coasts, which are not far from each other, a common undulation is observed.
- 6. The secondary undulations in many bays change their periods continuously and through certain ranges.
- 7. In some bays the periods of the undulation are fairly constant.
- 8. In many cases the same trains of secondary undulations appear in the same phase with respect to the tidal wave, on consecutive days of ordinary weather.
- 9. The phases of the prominent, fundamental undulation at different parts of a bay are equal.
- 10. The periods T of the most pronounced undulations are fairly given by the relation

$$T = \frac{4l}{\sqrt{gh}},$$

where l is the length of the bay measured along its depth, h the mean depth of the bay, and g the force of gravity.

11. Just outside a bay the undulation, which inside has been observed to be of considerable amplitude, may also be traced, but its amplitude is very small.

12. In a bay, the periods of the conspicuous undulation observable in the case of a storm, or in that of a seawave of distant origin, are the same as those ordinarily observable in the bay.

It has long been believed that the secondary undulation in a bay is the seiche between two opposite sides of the bay; but according to our observations, the phases of the most conspicuous undulation are the same throughout the bay, so that this view cannot be universally true. Napier Denison considers the undulation to be long waves continued from the ocean into the bay, on which supposition all the conclusions above enumerated, except the 9th, 10th, and 12th, can easily be explained. But the fact that there is a prominent undulation peculiar to each bay, cannot be explained by merely considering progressive waves.

This undulation, however, can be explained in the following way. As a representative example, take a rectangular bay

of constant depth. Suppose a regular series of long waves are continuously propagated in the direction of the length of the bay and are reflected at its end. Through the interference of the incident and reflected waves, a standing wave is formed having its loop of the vertical motion at the end of the bay. If the wave-length be such as to form the node of the vertical motion at the mouth of the bay, the period is the same as that of the fundamental oscillation of a tank having double the length of the bay; and therefore the amplitude of oscillation must necessarily be magnified by the successive occurrences of the long waves. The period of the oscillation is then, neglecting the mouth correction, expressed by the relation

$$T = \frac{4l}{\sqrt{gh}},$$

where  $\sqrt{gh}$  is the velocity of the long wave. This action of the bay may then be suggestively compared to the experiment in which a column of air in a resonance tube is made to vibrate in unison with a tuning-fork placed over its mouth.

If the waves of different periods proceed from the ocean toward the shore, the one whose period coincides with that of the oscillation having its node at the mouth of the bay will excite the most energetic oscillation of the bay water. Thus, bays on the coast-line may be compared with a series of resonators, each of which takes up selectively from the chaos of very complicated sounds or noises and resonates to the note of its proper period. The plausibility of such a conception seems to be heightened to a rather unexpected degree by the present investigation. Moreover, the fact that the rising and falling motion of the level of the bay in respect to the principal undulation is in the same phase for several stations, stands in favour of the above view. Darwin and Otto Krümmel\* seem to have entertained an analogous idea.

In a bay, besides the uninodal oscillation above referred to, oscillations with two nodes, three nodes, &c., are also possible; the periods of these oscillations are respectively  $\frac{1}{3}$ , &c. of the period of the fundamental oscillation. In some cases, a lateral oscillation of the bay excited by incident waves is also possible, the period of which is principally determined by the oscillating water in the bay. These additional modes of oscillation were actually found to exist in some bays such as Hososhima, Ôfunato, Hakodate, &c.

<sup>\*</sup> Darwin: 'The Tide,' ch. x. p. 169. Otto Krümmel: "Ueber Gezeitenwellen," Rede bei Antritt d. Rectorates d. Königl. Christ-Albr.-Univ. zu Kiel, März 5, 1897.

In the oscillation of the bay-water just referred to the period of the forcing wave, which corresponds to the maximum resonance, is not sharply defined, but within a small range the oscillation remains fairly conspicuous, as we have often

proved.

In the bays of regular shape, such as Ofunato and Hososhima, the position of the mouth line is determinate; but in the bays of complex shape, such as Shimoda and Susaki, several mouth lines are conceivable. By the choice of the mouth lines, the length and mean depth of the bay vary within a considerable range, so that the period of the proper oscillation changes within a certain range. Hence such a bay may resonate to any one of the incident waves whose period falls within the same range. In the two bays above mentioned, the period of the conspicuous undulation was

actually found to vary within a wide range.

As to the cause of the long waves, which manifest themselves as secondary undulations, we may mention the wind. the cyclone, the earthquake, &c. It is a matter of fact that the seiche in many lakes, which is the result of interference of direct and reflected waves of long wave-length, is often excited by a strong wind. In the same way the wind blowing on the surface of the ocean may cause long waves of several kilometres. Such waves, too, are often caused by a deep evelonic centre. Near such a centre fluctuations of pressure and of wind velocity go on incessantly, and these varying influences, acting in an impulsive way, may cause waves of long periods. An upheaval or depression of the sea-bottom, due to an earthquake or to a submarine eruption, may also be a cause producing the same result.

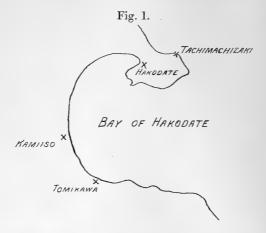
#### § 3. Results in Detail.

In the present abstract, it is not proposed to give the details of observations made at all the stations; we will confine ourselves to mentioning some of the remarkable findings in the bays, in which the secondary undulations appeared most markedly, and out of the sixty stations at which operations were carried on, we have chosen the following:

#### (i.) Hakodate.

Hakodate. situated on the middle coast of the strait of Tsugaru, which separates Hokkaidô from Honshiu, is the best anchorage in Hokkaidô. The bay is approximately semi-circular in shape. Here Kelvin's tide-gauge has been continuously working during the last twenty years, and has

recorded several important sea-waves which had their origin near the American coasts of the Pacific, as well as near our coasts.



At Hakodate the secondary undulations are very prominent, sometimes exceeding 30 cms. in amplitude, and of fairly regular periods. The periods \* of the most conspicuous range from 45<sup>m·5</sup>–57<sup>m·5</sup>. Sometimes its octave 21<sup>m·9</sup>–24<sup>m·5</sup> is found superposed on the undulation of the above period. In the undulation accompanying the sea-waves the octave

generally appears in a marked degree.

When observations at Hakodate and Kamiiso were carried on simultaneously, it was found that only the fundamental oscillation appeared on the records. The comparison of our records showed that the phase of the undulations was the same for these two stations. When like observations were made simultaneously at Hakodate and Tachimachizaki, it was noticed that although the conspicuous undulation appeared in the bay, yet just outside it was very insignificant. These observations agree well with our view regarding the secondary undulations, which we have propounded in the foregoing Section.

If we consider the longer period to correspond to the fundamental oscillation, and the shorter period to the lateral oscillation of the bay, the calculated periods for these oscillations are respectively 45<sup>m·3</sup> and 23<sup>m·6</sup>, which coincide well with the observed values. As we shall see hereafter, the periods corresponding to these two modes of oscillation, as given by our model of the bay, are also 47<sup>m·0</sup> and 23<sup>m·6</sup>.

<sup>\*</sup> Figures in heavy type always represent conspicuous undulations.

These results confirm our view regarding the nature of the

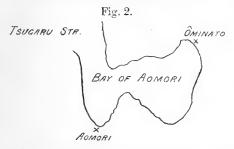
secondary undulation.

The amplitude of the secondary undulation is usually increased by a low barometric pressure, which is approaching the bay. As a good example, we may cite the cyclone of Sept. 21–22, 1904, which was approaching from the Pacific side of Honshiu toward Hakodate. The undulations in the bay continued over a whole day, with a considerable amplitude—the maximum exceeding 40 cms. The periods of conspicuous undulation were  $47^{m\cdot1}-56^{m\cdot9}$  and their octaves.

The bay is especially sensitive to sea-waves; and it is remarkable that waves originating on the American coasts have often been recorded by the tide-gauge of the bay. The periods of the Ecuador wave, 1906, in the bay were 24<sup>m·2</sup>–26<sup>m·0</sup> and 48<sup>m·3</sup>–51<sup>m·8</sup>; while those of the Valparaiso one were 23<sup>m·5</sup>–26<sup>m·0</sup> and 47<sup>m·0</sup>–52<sup>m·0</sup>. The periods of the great sea-wave of Sanriku, 1896, observed in the bay, were 23<sup>m·6</sup> and 47<sup>m·3</sup>–52<sup>m·1</sup>; those of the small wave, 1897, in the same bay were 22<sup>m·1</sup> and 45<sup>m·5</sup>.

#### (ii.) Aomori.

The large bay of Aomori has the form of a dumb-bell, and is connected with the strait of Tsugaru by a wide neck. The observations were made at Aomori, when the centre of a deep, low pressure was approaching the district from the Japansea side. On this occasion a regular undulation of 103<sup>m</sup>



appeared on the record and continued for a day and a half. Upon this an undulation of a period ranging from 23<sup>m</sup>·4 to 26<sup>m</sup>·3 was superposed. Besides, a period of 295<sup>m</sup> could also be traced.

The undulation of 103<sup>m</sup> is probably the lateral oscillation of the bay, and that of 295<sup>m</sup> the fundamental oscillation having its node at the mouth. The calculated periods 108<sup>m</sup> and 284<sup>m</sup> are thus in a fair agreement with these observed periods. The corresponding periods as given by our model

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are respectively 108<sup>m</sup> and 303<sup>m</sup>. The undulation of the shortest period may be the higher mode of the lateral oscillation.

### (iii.) Ûfunato.

The bay of Ofunato has an elongated form, and is somewhat crooked near its mouth, so that at Ofunato, which is situated at the end of the bay, the sea is extremely calm.



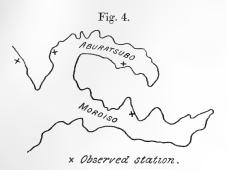
This affords a good example for illustrating the effect of shadow, *i. e.* a wave whose wave-length is large compared with the size of the obstacle goes round it, but a wave whose wave-length is comparatively small has its influence nullified by the obstacle, and the sea behind it remains quite calm.

The form of the bay is specially adapted to permit of comparison of the phases of the secondary undulations at different stations along its length; those chosen were Ôfunato, Sunagosaki, Takonoura, and Hosoura. The periods observed are 5<sup>m·5</sup>, 12<sup>m·8</sup>–16<sup>m·8</sup>, 36<sup>m·0</sup>–39<sup>m·1</sup>, and 41<sup>m·5</sup>–43<sup>m·5</sup>. The phase of the significant undulation 36<sup>m·0</sup>–39<sup>m·1</sup> is found to be the same for these four stations; which undulation is probably the fundamental oscillation of the bay. The calculated period is 36<sup>m·4</sup>—in close agreement with the observed.

At Ôfunato and Hosoura, where an undulation of the period 12<sup>m</sup>·8-16<sup>m</sup>·8 was sometimes observed, its phases were opposite to each other. The undulation was quite imperceptible at Sunagosaki, which is situated about midway between Ôfunato and Hosoura, so that this may probably be a binodal oscillation of the bay. Waves of the short period 5<sup>m</sup>·5 appeared at Hosoura and Sunagosaki, but not at Takonoura and Ôfunato; the absence of the wave at the latter stations is possibly due to the effect of shadow.

#### (iv.) Moroiso.

About 4 km. north of Misaki, in the province of Sagami, there lies a small forked bay, the one branch of which is called Moroiso, the other Aburatsubo. In Aburatsubo a Kelvin's tide-gauge is constantly working, the records of



which Professor F. Omori has frequently referred to as Misaki mareogram. The undulation is very regular and marked, having the period 13<sup>m</sup>·8-15<sup>m</sup>·6; the calculation of the period for the fundamental oscillation gives a fairly coincident value 13<sup>m</sup>·4.

The record shows an appearance of the beat of two waves of nearly the same wave-length. So it was suspected that the phenomenon might be due to the interference of the two distinct modes of oscillations of the two branches of the bay, which constitutes a vibrating system with two degrees of freedom. But this was found not to be the case, since the simultaneous observations at different parts of the bay showed the identity of the undulations with respect to their forms and phases. By comparing the records of the simultaneous observations at the inside and outside of the bay, we could distinctly trace corresponding undulations in the two records. The amplitude of the wave outside the bay is, however, very small as compared with that of the undulation inside the bay.

#### (v.) Susaki.

Susaki is a deep bay on the middle coast of Tosa in Shikoku. In it the observations were made at four stations—Yamasakibana, Ôtani, Heshima, and Kure. The diagrams of Yamasakibana are very conspicuous, and characterized by the simplicity of the undulations; the periods observed are 30<sup>m·9</sup>, 35<sup>m·4</sup>–38<sup>m·5</sup>, 40<sup>m·0</sup>–46<sup>m·8</sup>, and 50<sup>m·0</sup>–54<sup>m·0</sup>. The periods observed at Ôtani are 17<sup>m·6</sup>–18<sup>m·2</sup>, 35<sup>m·4</sup> and 53<sup>m·3</sup>; Phil. Mag. S. 6. Vol. 15. No. 85. Jan. 1908.

98 Messrs. K. Honda, T. Terada, and D. Isitani on the those at Heshima 24<sup>m·6</sup>-27<sup>m·6</sup>, 39<sup>m·7</sup>, and 55<sup>m·1</sup>. At Kure secondary undulations of the periods 15<sup>m·0</sup>-16<sup>m·3</sup> and 61<sup>m·3</sup>



were noticeable. Here it is to be observed that at the last three stations the records are not so rich in results as those at Yamasakibana.

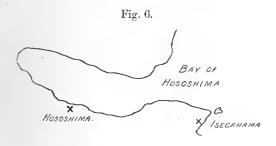
Comparing the records of Kure and Yamasakibana taken on the same days, it will be seen that the waves with the periods  $35^{\text{m}}-40^{\text{m}}$  appeared only at the latter station, and those of  $16^{\text{m}}$  only at the former. Again, comparing the records of Yamasakibana and Ôtani of the same days, the waves of  $35^{\text{m}}-40^{\text{m}}$  are found common in both stations, while waves of  $18^{\text{m}}$  are peculiar only to the latter. At Heshima, which is situated at the mouth of the minor inlet of Ôtani, waves of  $16^{\text{m}}$  are noticeable by their absence, while waves of  $35^{\text{m}}-40$  are apparently traced, though not of so great amplitude as at Yamasakibana.

Thus, we may infer that the undulation of  $35^{\text{m}}-40^{\text{m}}$  is the fundamental oscillation of the bay, having its node near Kure, and that the undulation of  $16^{\text{m}}$  at Kure is the oscillation of the minor inlet. The undulation of  $18^{\text{m}}$  at Otani is

probably the seiches between Awa and Ôtani. Calculated periods, corresponding to those supposed modes of oscillation, show a fair agreement with the actual periods. The experiments with the model also lead to the same conclusion.

#### (vi.) Hososhima.

Hososhima is an elongated bay on the eastern coast of Hiuga in Kiushiu; here Kelvin's tide-gauge is constantly working. It recorded several sea-waves, which were originated on the American coasts and which had travelled across the Pacific. Simultaneous observations were recorded at Hososhima and Isegahama, situated inside and outside the bay respectively. In the bay, extremely regular undulations



appeared superposed on the tidal wave, whose periods varied from 17<sup>m·8</sup> to 20<sup>m·3</sup> according to the tidal phase. In calm weather the amplitude of undulation amounted even to 25 cm. The period of the undulation slightly decreased as the tide passed from low water to high. The fundamental period, calculated to be 19<sup>m·0</sup>, agrees well with the observed one. The change of the period caused by a change of depth due to tidal influence, has also the range which is to be expected from the theory. Besides, longer periods such as 34<sup>m·0</sup>–38<sup>m·7</sup> and 43<sup>m·4</sup>–49<sup>m·1</sup> are sometimes observed.

Outside the bay, the undulation of the period  $17^{\text{m}}\cdot 8-20^{\text{m}}\cdot 3$  is very faint, while the undulations of the longer periods are barely observable. By placing the diagram of a record taken in the bay upon the corresponding one taken on the open coast, we can distinctly trace undulations in the two records, which correspond to each other. If we bring the records of any two consecutive days into coincidence as regards the tidal phase, we observe the same succession of undulations.

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(vii.) Nagasaki.

Nagasaki is a well-known harbour on the western coast of Kiushiu; the observations were made near the end of the bay. Since March of 1905 a tide-gauge of our system has



been set up in the same place by the Office, and many

significant records obtained.

In the bay, the secondary undulation is so conspicuous that it is usually known as *abiki*. The observed periods are  $22^{m\cdot5}-25^{m\cdot2}$ ,  $32^{m\cdot0}$ ,  $34^{m\cdot5}-37^{m\cdot6}$ ,  $40^{m\cdot1}$ ,  $44^{m\cdot5}-45^{m\cdot2}$ ,  $53^{m\cdot6}$ , and  $69^{m\cdot0}-72^{m\cdot0}$ ; the amplitude of the conspicuous undulations often exceeds half a metre. On one occasion, about ten years ago, the amplitude of the *abiki* was over 2 metres, and a large number of boats and steamers are said to have been damaged. The largest amplitude since the beginning of the tide-gauge observation was 1.54 m. observed on May 2, 1905. Pl. III. contains the record of the famous *abiki*.

The conspicuous *abiki* is generally associated with weathers in which the isobars in the neighbourhood trace a devious course, because of the co-existing low barometric centres. Since it is well known that a tornado is frequently associated with such a distribution of isobars, it seems then very probable that in such a weather a sudden local disturbance of

pressure may often occur, and that this barometric disturbance, giving rise as it does to waves of considerable length, may be a cause of the *abiki*. A deep barometric centre with regular concentric isobars, which is approaching the district, excites short waves of considerable amplitude, but does not cause an *abiki* of a marked amplitude.

As to the modes of oscillation of the bay, two are conceivable. The one is the seiches between the Fukahori side and the end of the bay; the other the fundamental oscillation having its node at the mouth. The periods calculated on this supposition are 22<sup>m</sup>·6 and 37<sup>m</sup>·5 respectively, in good agreement with the observed periods: experiments

with the model gave also fairly coincident values.

Near the western mouth of the bay of Nagasaki lies Fukahori, where Kelvin's tide-gauge incessantly operates. The undulation is generally imperceptible; the same periods as those at Nagasaki are also traceable. It is interesting to note that, though the uninodal oscillation of the bay is very prominent at Nagasaki, it is not especially so at Fukahori, the latter being situated near the node of the oscillation. Even the great abiki of Nagasaki on May 2, 1905, was only 30 cm. in amplitude at Fukahori. On the other hand, the seiches between Nagasaki and Fukahori sides are conspicuous even at the latter station, where the oscillation nearly forms the loop.

#### § 4. Experiments with Models.

To confirm our theory, we decided to experiment with models, in order to endeavour to find the actual mode of oscillation of the bay. Several models of bays were made exactly proportionate to the original, and the periods of the oscillating water in these models were compared with the observed ones. In reducing the period of oscillation in the model to the actual one, it was assumed that the period is proportional to its length, and inversely proportional to the square root of its depth, provided the latter is a small fraction of the former.

The construction of a model proceeded thus: first, contourlines of the bed of the bay to be modelled were drawn on separate zinc plates, and these plates cut along these lines. They were then placed one above the other, the space between each two being kept by blocks of wood of such thickness that the ratio to the actual depth was in each case maintained. The interspace between the plates was then filled with cement. The model thus constructed was immersed in a large rectan-

gular tank  $(150 \times 76 \times 19 \text{ cm.}^3)$  filled with water to the water-line of the model.

The waves were then excited by a pendulum-bob oscillating in the water. This was a lead ball, 7 cm. in diameter, suspended at the end of two pieces of cord, which from the point of suspension above passed downward through two holes in a movable horizontal bar, the latter being used to regulate the effective length of the pendulum. The part of the pendulum which oscillated with the bob was thus restricted to that part of the strings below the horizontal rod, the length of which could be varied at will by moving the rod upward and downward. With the pendulum arrangement, it was easy to obtain a period less than three seconds, but if one wished to obtain a longer period it would be necessary to use a pendulum of a considerable length. To avoid this inconvenience a horizontal pendulum was utilized. This was constructed by taking a horizontal brass bar, the one end of which rested in a steel cup embedded in a vertical framework, while the other was held by a cord which sloped from a point at the top of this framework. The cord was here attached by means of a steel ring, which rested on a knife-edge. A heavy lead ball was then suspended on the end of three strings from a frame attached to the movable end of the horizontal rod. By properly inclining this vertical framework, periods larger than three seconds could easily be obtained.

When the pendulum was made to oscillate in front of the model with its bob under the surface of the water, the water in the model oscillated smoothly, with no appreciable surface waves. In order to keep the amplitude of pendulum oscillation constant, a slight force by hand was applied near the upper end of the pendulum at suitable intervals. To avoid the reflexion of the excited wave from the walls of the tank, a thick layer of a damping material, such as wood-shavings,

was laid in front of the reflecting walls.

By simply exciting waves with the above arrangement, the water in the model made a standing oscillation, whose amplitude was generally small; but as the period of the pendulum approached to the proper period of the bay, the amplitude of oscillation gradually increased; and when the period of the pendulum coincided with this proper period, its amplitude was a maximum. In this case the mode of oscillation was the same as that conceived by us, that is, the end of the bay was a loop for the vertical motion, and a node for horizontal motion; while its mouth was a node for vertical motion, and a loop for horizontal motion. The

phase of the water particles in the bay was the same for all parts of the bay when the oscillation was fundamental. In an elongated bay, a binodal or trinodal oscillation was easily

produced.

It was convenient for the observation of the mode of oscillation to follow the motion of the fine cork powder, or better, fine aluminium powder which had been scattered over the surface of the water. To diminish the effect of surface tension of water as much as possible, a few drops of oil were poured on the water in the tank; but before the fine powder was scattered over it, the water was well stirred. way the path along which the water particles moved could be easily traced. We also took the photograph of the model in the tank, when the bay water was oscillating. By placing a camera in a vertical position over the model and giving an exposure equal to about half the time of a period of oscillation, a photograph was made on which could be traced the path of each moving aluminium particle; the aggregate of these paths then showed convincingly the actual mode of the horizontal motion.

To determine the proper period of oscillation of a bay, the period of the pendulum was so adjusted as to give a nearly maximum amplitude of oscillation. The pendulum was then stopped, and the period of the subsequent oscillations was determined by means of a stop-watch. Though the period of the pendulum varied slightly from the above value, the period of the subsequent oscillation was quite constant. If the period of the exciter differed considerably from the proper period of the bay, the oscillation after the stopping of the pendulum was rapidly damped, and this gave us a good means of detecting whether the period of the exciter was near to the proper one, or not.

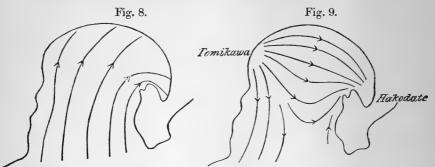
We experimented with models of seven bays, in which regular and conspicuous undulations were observed: the

results for three of these are given below :-

#### (i.) Bay of Hakodate.

The dimensions of the model were as follows:—Length 1:20200, and depth 1:548, so that the factor r, by which the observed period in the model must be multiplied in order to obtain the period of oscillation of the actual bay, was 863. The bay had two modes of oscillation: the fundamental, with its node at the mouth of the bay, and the lateral, which oscillated between Hakodate and Tomikawa with its node midway between. The periods of these oscillations were  $3^{\circ}\cdot 27$  and  $1^{\circ}\cdot 64$  respectively; multiplying by r we get  $47^{\circ}\cdot 0$ 

and  $23^{m\cdot6}$  in good agreement with the observed values. These two modes of oscillation were clearly seen from the photographs taken in the way before described. Figs. 8 and 9 of the annexed cut are the stream-lines traced on the



photographs. It is exceedingly interesting to trace the stream-lines in the case of the lateral oscillation. Certain of these lines extend from Hakodate to Tomikawa gradually diverting towards the middle, while other lines run toward the mouth of the bay from the Tomikawa side. Fig. 1 in Pl. IV. is a photograph of the fundamental oscillation of the bay.

In experimenting with models, it was observed that the period of the forcing wave, which corresponded to the maximum resonance, was not well defined; within a certain range of the period, which did not much differ from the period of free oscillation, the oscillation remained fairly conspicuous. In the actual case such a phenomenon was also observed: conspicuous undulations of  $45^{\text{m}} \cdot 5 - 57^{\text{m}} \cdot 5$  were frequently observed, though the period of free oscillation of the bay is  $47^{\text{m}} \cdot 0$ .

#### (ii.) Bay of Aomori.

The dimensions of the model were as follows:—Length 1:110700, and depth 1:731, so that the factor r was 4090.

This bay had also two modes of oscillation, as in the Bay of Hakodate: the fundamental and the lateral oscillation. The periods of these oscillations were  $4^{s}$ -45 and  $1^{s}$ -60 respectively; multiplying by r we get  $303^{m}$  and  $108^{m}$ . During our observations, the oscillations of periods  $295^{m}$  and  $103^{m}$  were observed, which agree well with the above values.

Fig. 2 in Pl.IV. is a photograph of the lateral oscillation of the bay. Here the greater part of the stream-lines extends from Aomori to Ominato, while the other part runs from Aomori toward the mouth of the bay; the case is just analogous to the corresponding oscillation in the Bay of Hakodate.

#### (iii.) Bay of San Francisco.

During the last fifty years the tide-gauge at San Francisco has recorded several sea-waves originated at different coasts of the Pacific, the periods of which are 17<sup>m</sup>·3-19<sup>m</sup>·2, 24<sup>m</sup>·3-27<sup>m</sup>·8, 34<sup>m</sup>·3-41<sup>m</sup>·2, 47<sup>m</sup>·4 and 116<sup>m</sup>, of which the first is an octave of the third.

Now the bay is so irregular in shape that it is very difficult to find out by calculation what modes of oscillation correspond to the actual periods; hence a model \* was constructed and experiments made. The scale of proportion used was as follows:—Length 1:40000, and depth 1:366, so that the factor r was 2076. The model was too large to go in the tank, so it was placed in a small pool in the court of the University.

Since the greater part of the model was very shallow, the oscillation rapidly subsided when the exciting wave was stopped, so that the period was always determined by observing the maximum resonance of the bay. For the wave incident upon Golden Gate, the principal modes of oscillation of the water were those between West Berkeley and Sausalito sides. The remaining portion of the bay, including both ends, seems to have but little influence on these modes of oscillation.

By exciting waves of the periods ranging from 3s-1 to 3s.5, the water in the bay oscillated with the fundamental mode of oscillation, having its node near Golden Gate and its loop at West Berkeley side. The mode of oscillation most easily excited was a binodal seiche between the narrowest mouth-line and West Berkeley side. The period of the wave, which gave a maximum resonance to the binodal seiche of the bay, ranged from 1s.1 to 1s.4. By slightly changing the period of the wave, the corresponding displacement of nodal line was observed. We could also produce a trinodal seiche of the bay, the period of which was nearly 0s.8. Multiplying these periods by r, we get  $107^{\text{m}}-122^{\text{m}}$ ,  $38^{\text{m}}-48^{\text{m}}$ , and 28m. The period 116m, which in all probability corresponds to the fundamental oscillation of the bay, was actually observed in the bay in the case of the sea-wave of South America, 1868. The periods corresponding to the binodal and trinodal oscillations above described have often been observed in the bay.

In concluding the present section, it may not be out of

<sup>\*</sup> We used the chart published by the Washington Coast and Geodetic Survey and presented to Professor Omori by Dr. O. H. Tittmann, Superintendent of the Office.

place to mention some experiments in oscillations made with tanks. We tried many forms of vessels, but will venture to

describe only one of them.

A circular vessel of constant depth  $(\pi \times 15^2 \times 8 \text{ cm.}^3)$  made of sheet zinc was partially filled with water. On a table two indiarubber tubes, each about 20 cm. long, were laid some 30 cm. apart, parallel to each other. A wooden plate, on which the circular vessel rested, was set upon these tubes in a horizontal position. By moving the plate to and fro with different periods, we could produce any desired mode of oscillation. The aluminium powder was scattered over the surface of the water, and then the oscillations were photographed as usual. Pl. V. fig. 1, shows the stream-lines in the fundamental oscillation; Pl. V. fig. 2 and Pl. VI. fig. 1, those of the second and the third harmonics respectively. They clearly indicate how each water particle moves. The theoretical treatment of this tank motion is given in Lamb's 'Hydrodynamics.'

Next, instead of periodically moving the wooden plate, two diametrically opposite points on the wall of the vessel were held by the fingers and the zinc walls simultaneously pressed, both inward and outward, with a proper period. Pl. VI. fig. 2 indicates the stream-lines of the oscillating water thus started;  $\alpha$ ,  $\alpha$  the points touched by the fingers. These stream-lines formed a system of hyperbolas. Here it is to be remarked that in such a complex motion of water, it was impossible to judge by the naked eye what form these

stream-lines actually have.

Thus the above investigation affords a good method of experimentally solving some difficult problems in tank motion, for which mathematics so far has failed to be of avail.

## § 5. Formulæ for Calculating the Periods of the Oscillation in Bays.

The oscillation in a bay is nearly the same as the seiches in a symmetrical lake, each half of which has exactly the same form as the bay under consideration. The hydrodynamical condition at the mouth of the bay is, however, slightly different from that at the middle part of the lake. Hence the period of oscillation in the bay is not exactly the same as that in the symmetrical lake; this difference is here called the mouth correction. If this correction be known, the problem of finding the period of oscillation of the bay water reduces itself to that of finding the period of oscillation in the lake.

#### (i.) Rectangular bay of constant depth.

Let l and h be the length and the depth respectively of a rectangular bay of constant depth; then the period T of the free oscillation of the bay, which has its node at the mouth and its loop at the end, will be given by the formula

$$T = \frac{4l}{\sqrt{gh}}, \quad \dots \quad \dots \quad (1)$$

provided the correction due to the mouth be neglected. This correction may be approximately found in the following

Take the origin of the rectangular coordinates at the middle point on the mouth of the bay; x-axis in the direction of length, positive inwards, and y-axis upwards. Assume the vertical displacement  $\eta$  inside the bay to be given by

$$\eta = a \sin \frac{\pi x}{2l} \cos \frac{2\pi t}{T}.$$

If we neglect the vertical acceleration, we have

$$\eta = -h \frac{\partial \xi}{\partial x}$$

where  $\xi$  is the horizontal displacement; hence

$$\xi = a \frac{2l}{\pi h} \cos \frac{\pi x}{2l} \cos \frac{2\pi t}{T},$$

and

$$\dot{\xi} = -a \frac{4l}{Th} \cos \frac{\pi x}{2l} \sin \frac{2\pi t}{T}.$$

If b be the breadth of the bay, the kinetic and potential energies inside the bay are given by

K.E. = 
$$\frac{1}{2}\rho hb \int \dot{\xi}^2 dx$$
 and P.E. =  $\frac{1}{2}gb\rho \int \eta^2 dx$ ;

assume also the kinetic energy outside the bay to be  $Phb^2\rho\dot{\xi}_0^2$ , where  $\dot{\xi}_0$  is the value of  $\dot{\xi}$  at x=0,  $\rho$  the density of water, and P the dimension of a number. Neglect the potential energy outside the bay, which is very small, and write down the condition of the constancy of energy. From the two relations which are obtained by putting t=0 and  $t=\frac{T}{4}$  in this equality, we get the expression for the period of oscillation:—

$$T = \frac{4l}{\sqrt{a\bar{b}}} \left( 1 + 4P \frac{b}{\bar{l}} \right)^{\frac{1}{2}}. \qquad (2)$$

Lord Rayleigh \* found the reaction of air upon a vibrating rectangular piston, whose length y is very great compared with its breadth b, to be equal to the addition of a mass

$$y\frac{b^2}{\pi}\left(\frac{3}{2}-\gamma-\log\frac{\kappa b}{2}\right)$$

where  $\gamma = 0.5772$  and  $\kappa = \frac{2\pi}{\lambda}$ ,  $\lambda$  being the wave-length. If the reaction be uniform over the piston, we have for y = h

$$\frac{hb^2}{\pi} \left( \frac{3}{2} - \gamma - \log \frac{\kappa b}{2} \right).$$

Now, in a problem of long waves, we usually neglect vertical acceleration and consider horizontal acceleration nearly constant for different depths. Vertical planes, which are parallel to wave ridges and fixed relative to water, make a to-and-fro motion similar to the case of aerial vibration. The node of an aerial stationary wave corresponds to the loop of the water wave and vice versa. If we use the analogy for the expression of the kinetic energy, we have

$$P \doteq \frac{1}{\pi} \left( \frac{3}{2} - \gamma - \log \frac{\pi b}{\lambda} \right),$$
$$\doteq \frac{1}{\pi} \left( \frac{3}{2} - \gamma - \log \frac{\pi b}{4l} \right).$$

This relation seems to be sufficient for the estimation of the order of magnitude of the mouth correction.

#### (ii) Irregularly shaped bay.

Professor Chrystal<sup>†</sup>, in his hydrodynamical theory of seiches, has satisfactorily worked out the problem of seiches for irregularly shaped lakes. When the shape of a lake does not considerably differ from that of a rectangular tank, the following method of calculating the period may be of some practical importance, though not very rigorous.

Consider a nearly rectangular lake of the length l and the mean transverse section  $S_0$ . The section  $S = S_0 + \Delta S$  varies slightly such that square of  $\Delta S/S_0$  may be neglected in comparison with unity. If the variation of S be everywhere gradual, we may assume that the horizontal displacement of water in every section is in the direction of the

<sup>\*</sup> Lord Rayleigh, Phil. Mag. vol. viii. 1904. † Chrystal, Trans. Roy. Soc. Edin. vol. xli. 1905.

length of the lake and also uniform in each section. The vertical acceleration is neglected in comparison with the

horizontal.

Take the origin of rectangular coordinates at one lend of the lake, x axis being in the direction of length.  $\xi$ ,  $\eta$ , b have the same meaning as before. Then the kinetic and the potential energy are given by

K.E. = 
$$\frac{1}{2}\int \rho S\dot{\xi}^2 dx$$
 and P.E. =  $\frac{1}{2}\int gb\rho\eta^2 dx$ ,

respectively. Again, from the condition of continuity,

$$b\eta = -\frac{\partial X}{\partial x},$$

where  $X=S\xi$ . By the condition of the constancy of energy, we have

$$\int_0^1 \frac{\dot{\mathbf{X}}^2}{\mathbf{S}} dx + g \int_0^1 \frac{1}{b} \left( \frac{\partial \mathbf{X}}{\partial x} \right)^2 dx = \text{const.}$$

Assuming for the first approximation

$$X = a \sin \frac{\pi x}{l} \cos nt,$$

substituting this value in the above equality, and putting t=0 and  $t=\frac{T}{4}$ , two relations are obtained; whence the expression for the period of oscillation follows at once:—

$$T = \frac{2l}{\sqrt{gh_0}} \left\{ 1 + \frac{1}{2l} \int_0^l \cos \frac{2\pi x}{l} \left( \frac{\Delta b}{b_0} + \frac{\Delta S}{S_0} \right) \right\}, \quad (3)$$

where  $lb_0$  = surface-area and  $h_0b_0$  =  $S_0$ . Here the expression

$$\Delta l = \frac{1}{2} \int_{0}^{l} \cos \frac{2\pi x}{l} \left( \frac{\Delta b}{b_0} + \frac{\Delta S}{S_0} \right) dx$$

may be considered as the correction to the length. It shows that any contraction or expansion towards the central part of the lake prolongs or shortens its natural period respectively, and that a contraction or expansion towards the ends

shortens or prolongs it respectively.

To apply the above expression in the case of a bay, we need only to consider a lake whose shape is symmetrical with respect to the vertical plane through the mouth line, and to find the period of the seiches in the lake by the above formula. This period, if it be corrected for the mouth, is the required period of oscillation in the bay.

#### (iii.) Dumbbell-shaped bay.

The above formula does not hold when a portion of the lake is very much contracted. In this case, then, we may

treat the problem in a quite different way.

When two basins communicate with each other by a narrow canal, the mode of oscillation of the longest period takes place when the levels of the two basins rise and fall alternately. If the breadth of the canal be very narrow compared with the dimensions of the two basins, we may assume that the rise and fall of the level are uniform for each basin, and that in the canal the level is invariable, the motion of the water being chiefly horizontal. Then, denoting the areas of the basins by S and S', the breadth, the depth, and the length of the canal by b, h, and l respectively, the displacement of water in the canal in its direction by  $\xi$ , and the vertical displacement of the surface of S and S' by  $\eta$  and  $\eta'$  respectively, the potential and the kinetic energy are given by

P.E. = 
$$\frac{\rho g}{2} (S\eta^2 + S'\eta'^2)$$
, and K.E. =  $\frac{\rho bhl}{2} \dot{\xi}^2$ .

Again, the correction to the kinetic energy on each end of the canal is nearly

$$\frac{\rho h b^2}{\pi} \left( \frac{3}{2} - \gamma - \log \frac{\pi b}{\lambda} \right) \dot{\xi}^2,$$

in which  $\lambda$  is the wave-length, if the basins be infinitely wide, and may be considered nearly equal to four times the length of the basin in the direction of oscillation.

Since 
$$S\eta = -S'\eta'$$
 and  $S\eta = bh\xi$ ,

we obtain in the usual manner for the period of oscillation

$$T = 2\pi \sqrt{\frac{Sl}{gbl\left(1 + \frac{S}{S'}\right)} \left\{1 + \frac{2b}{\pi l}\left(\frac{3}{2} - \gamma - \log\frac{\pi b}{\sqrt{\lambda \lambda'}}\right)\right\}}.$$
 (4)

Special interest is due to the case when one of the basins becomes infinitely large; in which case the problem reduces itself to that of a bay communicating with the open sea through a narrow neck. Taking  $\lambda = \lambda' = 4L$ , where L is the length of the bay measured along the probable direction of propagation of waves, we obtain from the above equation,

$$T = 2\pi \sqrt{\frac{8l}{gbh}} \left\{ 1 + \frac{2b}{\pi l} \left( 0.923 + \log \frac{4L}{\pi b} \right) \right\}. \quad (5)$$

# § 6. Method and Results of Determining the Period of Oscillation by Calculation.

In the calculation of the period of oscillation in a bay by the simplest formula, it was necessary to estimate the length and the mean depth of the bay from the charts; the charts used were those published by the hydrographical section of the Naval Department. As the mean depth, we took the ratio of the total volume of the water in a bay to the area of the surface. The length of the bay was measured along a line drawn lengthwise and perpendicular to the contour-lines of the bed of the bay.

To find the mean depth of a bay, we began by drawing contours on the chart, where the depths at a number of points referring to low-water springs are given. After drawing as many contours as the case requires, we measure with a planimeter the areas between them. These areas multiplied by the corresponding depths, increased if necessary by the half range, give the partial volumes of water. Dividing the sum of these partial volumes by the area of the free surface, we get the mean depth.

We calculated by formula (1) the periods for all observed bays. For several typical bays we also calculated the correction due to the change of the section, as well as that due to the mouth, and compared the corrected values with the observed.

The calculation of the correction due to the variation of the section was carried out in the following way. We drew on the chart several lines at suitable positions normal to the line of length, and then taking the length as abscissa and the corresponding breadth as ordinate, we got a breadth-diagram. We next drew the mean breadth-line at a distance equal to the whole surface of the bay divided by the length. Taking now this line as the new axis of coordinates, we could easily draw the diagram for  $\Delta b \cos \frac{2\pi x}{l}$ ; whence by mechan-

ical integration, we get the value of  $\int \Delta b \cos \frac{2\pi x}{l} dx$ . Proceeding in a similar way for the sectional area, we got the value of  $\int \Delta S \cos \frac{2\pi x}{l} dx$ . From these two the required correction was obtained by simple operations.

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The results of calculation of two corrections for three bays are given below:—

$4l\sqrt{gh_0}$ .	Corr. for section.	Corr. for mouth.	т.
213ա	+24·8 <sup>m</sup>	+46·5m	284 <sup>m</sup>
97.5	+ 8.5	0	106
39.5	-10.7	+ 8.6	36.4
60.0	-16.8	15.8	59.0
	213 <sup>m</sup> 97·5 39·5	213 <sup>m</sup> +24·8 <sup>m</sup> 97·5 + 8·5 39·5 -10·7	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

According to our investigation, the bay of Aomori oscillates in two different modes with the periods 295<sup>m</sup> and 103<sup>m</sup>. The longer period corresponds to the fundamental oscillation; while the shorter one corresponds to the lateral oscillation, for which the mouth correction is naturally zero. The last two bays in the above table are good examples, showing that the correction due to the section and that due to the mouth nearly cancel each other. Similar remarks apply for many other bays.

When the mouth of a bay is decidedly contracted, formula (1) or (3) fails to give the period of oscillation, in which case formula (5) is to be used. The bay of Osaka, which is almost surrounded by land and which communicates with the external sea through two necks, Akashiseto and Yuraseto, may be taken as an example of such bays.

For the resultant conductivity of necks, the sum of separate conductivities was duly taken. The data for the calculation of the period estimated from the chart is:—

Akashiseto ... 
$$b_1 = 3.9 \text{ km.}$$
,  $l_1 = 6.2 \text{ km.}$ ,  $h_1 = 41 \text{ m.}$ , Yuraseto .....  $b_2 = 5.0 \text{ km.}$ ,  $l_2 = 1.2 \text{ km.}$ ,  $h_2 = 27 \text{ m.}$ ,  $S = 1.47 \times 10^3 \text{ km.}^2$ ,  $\lambda = 150 \text{ km.}$ ;

whence by formula (5),  $T=270^{m}$ . This agrees nearly with the largest period observed,  $260^{m}$ — $310^{m}$ .

In the following table are given the periods calculated by formula (1) for all observed bays \*. The periods corrected for the variation of the section and for the mouth are given in heavy type. The letter S indicates that the periods which it follows are those for the lateral or seiche-like oscillation in the bays. In the table only the observed periods, that we

\* In the table, 1-5 are the bays along the coast of Hokkaidô, 6-9 those along the coast of Japan Sea, 10-25 those along the southern coast of Honshiu, 26 that in Shikoku, and 27-29 those along the coast of Kiushiu. Futami is a small bay in Bonin Island (Ogasawara), and Kiirun the sole harbour in Formosa.

considered to correspond to the calculated ones, are given side by side. It must be understood that for each bay there are many other periods observed, though not so conspicuous as those here quoted.

	Bay.	Observed Period.	Calculated Period.
1.	Otaru	13·8 <sup>m</sup> —16·5 <sup>m</sup>	17:3m
2.	Nemuro	10.9	9.0
3.	Hamanaka	49.5	48.2
4.	Mororan	51·1-54·0	48.9
5.	Hakodate	45.5-57.5	45.3
	,,	21.9 - 24.5	23.6 S
6.	Aomori	295	284
	,,	103	106 S
7.	Fushiki	54.1	52.7
8.	Tsuruga	56.7 - 62.9	59.0
9.	Tonoura	11.9-12.9	11.1
10.	Miyako		45.4
		21.3-22.0	24·0 S
11.	Kamaishi	24.8 - 26.0	24.8
		20.3	22.3
12.	Kojirohama	24.6	26.0
13.	Yoshihama	18.5-20.1	21.1
14.	Okirai	27.5 - 29.9	26.4
15.	Rvori	18.3	18.4
16.	Ôfunato	36.0-39.1	36.4
17.	Niiyama	6.4 - 7.6	7.5
18.	Ayukawa	6.8 - 8.9	8.9
19.	Moroiso	13.8 - 15.6	13.4
20.	Shimoda	13.8 - 18.2	13.3—15.9
21.	Ise Sea	390	363
22.	Mikawawan	208	217
23.	Kushimoto	16.5 - 18.6	18.3
	. ,,	11.6 - 13.0	12.8
24.	Ôsaka	260 - 310	270
	,,	106 - 150	126
	,,	6166	63
25.	Hiroshima	60.0	61.6
26.	Susaki	*****	39.1
	,,	17.6 - 18.2	16.0 S
	,,	15.0-16.3	17.0
27.	Hososhima	17.8 - 20.3	19.0
	,,	6.5 - 8.7	6.3
28.	Aburatsu	15.0-19.0	15.1.
29.	Nagasaki	34.5 - 37.6	37.5
	,,	22.5 - 25.2	22.6 S
30.	Futami	16.0 - 20.0	13.6
31.	Kiirun	25.3 - 29.6	25.8

It will be seen from the table that in most cases, the periods calculated by the simplest formula (1), that is,

$$T = \frac{4l}{\sqrt{gh}},$$

agree fairly well with those actually observed. Thus for *Phil. Mag.* S. 6. Vol. 15. No. 85. *Jan.* 1908.

many cases the corrections due to the mouth and the variation of the section seem to be superfluous. This probably arises from the fact that in many bays the correction due to the section nearly cancels the correction due to the mouth; for such bays gradually contract and the depth decreases as we approach the end, therefore the correction due to the variation of the section is negative, and the mouth correction being always positive, the two tend to annul each other. a good example, we may refer to the bays of Ofunato and Tsuruga. If, however, the mouth of a bay be contracted and shallower than the inside, the correction due to the section is positive, and the total correction may, in some cases, amount to a considerable quantity. In such cases, the value calculated by the simplest formula must be decidedly less than the observed value, and can be brought into agreement only by taking the two corrections into consideration; a good example of this is furnished in the case of the bay of Aomori. That the calculated periods for the bays of Mororan and Okirai, both of which have rather narrow mouths, are a little less than the observed values, is also explained on the same view.

#### § 7. Sea-Waves and Secondary Undulations.

As already remarked, Professor F. Omori found that the periods of sea-waves observed in a bay are the same as those of the usual secondary undulation. We have made a like investigation for different bays, and our findings confirm his conclusion, especially in the case of sea-waves of distant origin. This fact now may be explained in the following way.

Sea-waves are probably of such a complex nature, as to be represented by the sum of a series of long waves of different periods and amplitudes. If a group of these waves proceed towards a bay, the bay takes up and resonates to the undulation whose period coincides with that of the free oscillation of the bay. Thus the prominent undulation in a bay, whatever the component waves of a sea-wave may be, is the undulation whose period is nearest to that of the free oscillation.

The above consideration applies chiefly to sea-waves that are of distant origin, and consequently of small amplitude. If, however, the origin is not very far from a bay or an open coast, progressive waves of long wave-length, irrespective of their periods, are sufficient to cause a disastrous effect on the coast; for by Green's law of amplitudes, long waves considerably increase their amplitude the nearer they approach a shallow shore. Thus it is that the report on actually destructive sea-waves almost always speaks of high wave-fronts

approaching towards the shore, indicating that the waves are of the nature of progressive, but not of stationary oscillations. When that disastrous wave of 1896 visited our coast of Sanriku, there were instances in which the periods of the wave did not coincide with those observed in ordinary cases.

In the investigation of the nature of sea-waves, the tide-gauge is at present the sole instrument available; and in order to obtain the best results it should be set up where there is an open coast, or better in the neighbourhood of a small isolated island. If the instrument be placed in a calm bay, as is usually done, the waves are much modified by the proper oscillation of the bay.

In the following pages discussions relative to sea-waves,

originated from three different causes, will be given.

#### (i.) Sea-waves of the Krakatoa Eruption, 1883.

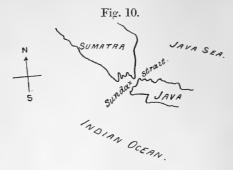
Great sea-waves caused by the eruption of Krakatoa, August 27, 1883, swept over the entire area of the Indian Ocean, and even forced their way as far as the northern parts of the Atlantic and the Pacific, leaving as they went evidence of their visit on all intervening tide-gauges. These records have been published in the Report of the Royal Society of 1888, and described by Captain W. J. H. Wharton.

As to the cause of the periods of these great Krakatoa waves, few theories have been proposed. Captain Wharton \* attempted to explain the period of two hours by assuming that the sea-bottom was upheaved for about an hour. According to Professor H. Nagaoka †, the earth is continually vibrating to the period 67<sup>m</sup>, which is the period of the fundamental oscillation; and this vibration was what actually determined the periods of the Krakatoa waves. Our theory differs from the above by not assuming the slow up and down motion of the sea-bottom. Now any portion of the sea partly bound by land, if suddenly excited by some great disturbing cause, oscillates with its own stationary mode and may continue for some time after the cause of the excitement has disappeared. Sunda Strait, from the character of its boundaries, may be taken as a good example. The south-west end of the channel opens widely into the Indian Ocean, while the northeast end, which is very narrow and shallow, leads to the Java Sea. The strait, as a whole, may be compared, by an acoustical analogy, to a conical open pipe. The loop of the gravest

<sup>\*</sup> Wharton 'The Report of the Krakatoa Eruption,' p. 97.

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mode of oscillation possible in such a channel must lie midway through or perhaps somewhat nearer the narrower end.



Hence the eruption of Krakatoa which burst forth at the loop of this oscillation would be very favourable to excite natural, stationary oscillation of the strait as a whole. The initial disturbance would soon settle into a regular oscillation natural to the system, and this oscillation would be propagated into the external ocean as a train of regular waves, whose period is determined by that of the source.

Taking the length of the strait as 160 km. and its mean depth as 183 m., we obtain from our formula \* T=126m, which was actually recorded by the tide-gauge of Batavia. Besides the mode of oscillation above described, a binodal oscillation between the two sides of the strait, the Javan and Sumatra sides, might possibly be generated by the eruption, which occurred at the loop of this mode of oscillation also. The period of this oscillation is calculated to be about one hour, which nearly coincides with the periods recorded at many stations along the Indian coast. In addition, the modes of oscillation higher than the above two, with comparatively small amplitudes, might possibly have been in co-existence.

Beyond the north-east end of the strait the sea becomes shallow and the bed abounds in irregularities, which may cause a scattering of the waves that have been propagated from the end of the strait, through complicated reflexion and refraction. Besides, the sectional area of the north-east end of the strait is estimated to be about  $\frac{1}{60}$  that of the south-west end; so that the energy propagated from the former mouth must have been a small fraction of that from the latter. These considerations probably account for the smallness of the waves propagated in the north-eastern direction.

<sup>\*</sup> In this case, our formula evidently becomes  $T = \frac{2l}{\sqrt{gh}}$ ; because both ends are open.

The tide-gauge nearest Krakatoa at the time of the eruption was that of Batavia. It recorded two-hour waves, but not a trace of one-hour waves appeared. The absence of these latter, however, raises no serious objection against our supposition, because the narrow opening to the north-east of the strait is very unfavourable for the propagation of the energy of the lateral oscillation, much more so than for that

of the longitudinal.

Thus the major part of the energy of oscillations was propagated into the Indian Ocean, and left its record on the tide-gauges even so far distant as the ports of Southern Africa. Examining the records given in the above cited report, we may in general distinguish two types of undulations—the one those propagated directly from Krakatoa, and the other those of the stationary oscillation of bays or estuaries excited by the incident waves. Prominent undulations recorded along the coast of India belong to the former type. Comparing the records at Madras and Vizagapatam or Negapatam and Port Blair, an identity of waves may easily be recognized. We see also the trace of Vizagapatam waves in Nagapatam records, and vice versa. Most of these stations are not situated in either a bay or an estuary where an oscillation of such a long period is possible.

For remoter stations, we see in general that the disturbances are chiefly due to the second type, i. e., the proper oscillation excited by the synchronizing components of the incident waves. Hence for such bays the periods of oscillation for Krakatoa waves must coincide with those calculated from the dimensions of the bays. To verify this point we require reliable charts giving all necessary data; but having no such charts at hand, we had to be satisfied with deducing the mean depths of the different bays, quoted in the Krakatoa Report, from their periods of oscillation and their lengths estimated from charts \* available. The results of our calculation for Port Elizabeth, Table Bay, Port Adelaide, Port Phillip, Lyttleton, and Honolulu all gave reasonably mean depths,

when judged from the charts at hand.

#### (ii.) Sea-waves accompanying Earthquakes.

A number of great sea-waves caused by earthquakes have been recorded by the tide-gauges at different stations. We have studied these records, and found that the periods of the waves as given by the tide-gauge at a distant station are the

<sup>\*</sup> Berghaus, Physikalischer Atlas, Shuter's Atlas, and Encyclopedia Britannica.

same as those of the ordinary secondary undulations. In this connexion we quote a few of the most accurate records from modern occurrences.

On June 15, 1896, the most destructive and disastrous sea-wave of modern times visited the coasts of Sanriku in Japan. It originated in the sea about 150 km. off the coast of Sanriku, the product of a submarine earthquake, and soon assumed such proportions that at Yoshihama the height recorded was 24 m. It swept away many towns and villages along the coast of Sanriku covering a distance of about 320 km. In all 22,000 lives were sacrificed. The sea-wave also crossed the Pacific, reaching the western coast of America. It left its records on the tide-gauges of Honolulu and San Francisco.

In the following table the observed periods, together with those observable in ordinary cases, are given.

Station.	Sea-Wave.	Ordinary Undulation.
Hanasaki	7m	(Coast)
Hakodate	23 <sup>m</sup> ·6; 47 <sup>m</sup> ·3—52 <sup>m</sup> ·1	21 <sup>m·9</sup> —24 <sup>m·5</sup> ; 45 <sup>m·5</sup> —57 <sup>m·5</sup>
Miyako	8, 16	12; 21·3—22·0
Ayukawa	7-8	6.88.9
Chôshi	7	(Coast)
Moroiso	15	13.815.6
Honolulu	26.0-23.4	
San Francisco	6.2, 34.3	

Now, according to the results of our investigation, the periods of the principal sea-waves on the coast of Sanriku are 7<sup>m</sup>-8<sup>m</sup> and 15<sup>m</sup>-17<sup>m</sup>. The records of two coast-stations, Hanasaki in Hokkaido and Chôshi in Shimôsa, though they lie on opposite sides of Sanriku and are a considerable distance from each other, showed the existence of the same wave. At Miyako, which is the nearest station at which the sea-wave was scientifically observed, the periods of the wave were different from those in ordinary cases. Though actual observations are wanting, the same remark seems to apply to the places where the sea-wave produced its most disastrous effect. In distant bays, Hakodate and Moroiso, the periods of the wave are the same as those usually observed. The periods observed at Honolulu and San Francisco are also the same as those observable in the case of other sea-waves.

On February 1, 1906, in our time, a strong earthquake was

felt on the Pacific coast of Ecuador; it was accompanied by a sea-wave, which traversed the Pacific from America to Japan. The wave was recorded by the tide-gauges of Hakodate, Ayukawa, Kushimoto, and Hososhima. The earthquake of Valparaiso, which was also followed by a sea-wave, occurred on July 17 of the same year. The wave arrived at Hakodate, Ayukawa, and Kushimato. The above two waves also slightly affected the tide-gauges \* at San Francisco, San Diego, and Honolulu. The periods observed in these bays are:—

Bay.	Ecuador Wave.	Valparaiso Wave.	Ordinary Case.
Hakodate	51 <sup>m</sup> ·8—48 <sup>m</sup> ·3	47 <sup>m</sup> ·0—52 <sup>m</sup> ·0	45 <sup>m</sup> ·5—57 <sup>m</sup> ·5
,,	24.2-26.0	23.5—26.0	21.9—24.5
Ayukawa	7.3-8.3; 20	73; 23	6.8—8.9; 22
Kushimoto	21.0; 13.2	12.3; 21.4	11.6—13.0; 21.5—23.7
Hososhima	20.4		17.8—20.3
San Francisco	*******	25.3	
San Diego	16.7; 33.5	32.2; 43	-
Honolulu	24.8-26.8	26:2	
		}	

Thus in the bays on our coast the periods of the sea-waves are the same as those observed in ordinary cases. The periods observed at San Francisco and San Diego are those frequently observed in the case of other sea-waves; they correspond to the multinodal oscillations of these bays. The periods observed at Honolulu are quite constant; they possibly correspond to the fundamental oscillation in the inlet of Honolulu.

In passing, it is interesting to calculate the velocity of propagation of sea-waves through the Pacific. If the path of the sea-waves which travel across the Pacific be known, the velocity of propagation can be estimated. Now the sea-wave which has usually a long wave-length compared with the depth of the ocean, must be refracted according to the condition of the bottom, so that it is very difficult to know the actual path by which these waves travelled through the ocean. We therefore conceived several paths between the place where the waves originated and the observed station in question, and then we measured the lengths, and also the mean depths, of each by mechanical integration †. The velocity of propa-

<sup>\*</sup> The tide-gauge records utilized are those furnished by Dr. Tittmann to Prof. Omori.

<sup>+</sup> The chart published by "Deutsche Seewarte" was used.

gation of the long waves over each path was then calculated from the various mean depths. The times of transmission of the waves over each path were compared, and the path with the minimum time was taken to be the actual one. From the path thus found and the actual time of transmission, we calculated the mean velocity of propagation of the sea-wave, as given in the following tables. The time of the occurrence of the earthquake we took as the starting-time of the sea-wave.

#### Sanriku Wave.

Station.  Honolulu San Francisco .	Distance. 6000 km. 7970	Mean Depth *.  4.92 km.  5.51	√għ. 220 m./sec. 234	Time Interval.  7 <sup>h</sup> 44 <sup>m</sup> 10 <sup>h</sup> 34 <sup>m</sup>	Velocity.  216 m./sec. 209
Ecuador Wave.					
Hakodate Ayukawa Kushimoto Hososhima	" 15280	4·92 km. ,, 4·81	220 m./sec.	20 <sup>h</sup> 16 <sup>m</sup> 20 <sup>h</sup> 12 <sup>m</sup> 20 <sup>h</sup> 44 <sup>m</sup> 20 <sup>h</sup> 38 <sup>m</sup>	195 m./sec. 200 208 211
Valparaiso Wave.					
Hakodate Ayukawa Kushimoto	,•	4·66 km. ,, 4·58	214 m./sec. " 212	23h 48m 23h 17m 23h 31m	200 m./sec. 204 208

Hitherto it has been customary to measure the path of the sea-waves as supposedly lying along the great circle of the earth; but the actual distribution of the depth being complicated, this is not a proper method.

The value  $\sqrt{gh}$  of the fourth column in the above tables represents the theoretical velocity of long waves. This theoretical velocity is always greater than the actual mean velocity, but here the difference is not constant, while in one case it is very small, in another considerable. This fact has

<sup>\*</sup> One of us (K. Honda) calculated the mean depths of the ocean by the same method; but having used "Berghaus Physikalischer Atlas," the values were considerably greater than in the present case. See Proc. Tokyo Math.-Phys. Soc. iii. No. 9 (1906).

been noticed by several earlier writers, such as Milne, W. J. H. Wharton, E. Geinitz, C. Davison, &c. The point \* noticed by C. Davison as regards the mean velocity, if it be taken into account, does not diminish the discrepancy more than one per cent.

#### (iii.) Sea-waves accompanying Cyclonic Storms.

Disturbances of the sea-level caused by cyclonic storms produce phenomena which may be conveniently classified under three heads, namely, short waves; long waves; and the abnormal rise of sea-level.

The violent, short waves, commonly called in Japan Gekiro, have periods usually of a few minutes, and are superposed by waves of still shorter periods but of considerable amplitude. These waves are always associated with strong gales, and have

probably the same origin as ordinary wind-waves +.

As to the long waves, examples are very numerous in which secondary undulations of remarkable amplitude occur, accompanying the cyclonic centre which was passing the vicinity 1. In some cases remarkable undulations occur for a few hours, but soon abate into usual waves with the rapidly retreating cyclonic centres; while in other cases they last for one or two days with considerable amplitude. In any case, the periods of remarkable waves in a bay are generally the same as those observed on ordinary days. The period of the most prominent undulation, however, is different in different cases: in some the fundamental period is most pronounced, while in others one of the higher harmonics is conspicuous. Generally speaking, the duration, as also the period of the prominent undulation, seems to depend on the width, the velocity, and the distance of the cyclonic centre. Again, in many cases, especially for the Japan Sea coast, the periods of conspicuous waves accompanying cyclones in different stations and for different occasions are nearly similar. On the Japan Sea coast it is frequently found that a series of waves recorded at one station is quite similar in form to one obtained at another, distant station on a different occasion. Similar cases also appear with regard to the Pacific coast, though often masked by the undulation proper to the bays. In connexion with this fact, it will be noticed with interest that the wave-lengths of the most prevalent, cyclonic waves are generally comparable with the dimensions of the area of the cyclonic

<sup>\*</sup> Davison, Phil. Mag. vol. l. (1900). † Wheeler, 'Tides and Waves,' Ch. X.

<sup>1</sup> See also ibid. Ch. XI.

depression prevalent in our sea. It is in all probability true that the barometric fluctuations constantly going on at a cyclonic centre, acting in an impulsive way, may give rise to a train of long waves whose wave-lengths are comparable with the dimensions of the centre.

Abnormal upheavals of sea-level have also been frequently observed on our coast. In some cases the level gradually rose and fell with the passing cyclonic centre, while in others the sea was abruptly upheaved, apparently by the action of strong gales. On one occasion a considerable rise of the level was observed, when neither cyclone nor earthquake was reported.

It may be added here that in some bays remarkable secondary undulations occurred in ordinary calm weather, although there was no cyclone in the neighbouring sea. These undulations seem to be associated with the unstable distribution of atmospheric pressure. For example, the abnormal undulations in Nagasaki known as "abiki" are usually accompanied by devious isobars and twin-centres of low pressure.

#### § 8. Oscillation of large Bays and Anomaly of Tides.

Thus far we have generally discussed secondary undulations, the periods of which are much shorter than those of the principal tidal components, viz. the diurnal and semi-diurnal. We will now proceed to consider those undulations of much longer periods, that commonly exist in the tides of very large inlets or estuaries.

Exaggeration of oceanic tides, which takes place in shallow seas and in estuaries, has often been explained merely by Green's law of amplitude \*. Airy † attempted to explain anomalies of tides observed in some rivers, by the consideration that for a wave of finite amplitude different parts of the wave-profile travel with different velocities; but his argument has been proved untenable ‡. Again, inferior tidal components, known as compound tides or over-tides, which become conspicuous only in shallow basins, have been explained on the analogy of combination tones in acoustics §. It seems to us, however, that the theory alone is not sufficient to account for the facts that in some gulfs or bays the amplitudes of superior tides are often comparable with those of the proper tidal components, and also that most pronounced, compound tides

<sup>\*</sup> Green, Camb. Trans. vi. 1837; Math. Papers, p. 225.

<sup>†</sup> Airy, 'Tide and Waves,' Art. 198.

† McCowan, Phil. Mag. [5] xxxv., 1892.

§ W. Thomson, Proc. Roy. Soc. vii. G. H. Darwin, Brit. Assoc. Report, 188.

are different for different bays and gulfs. Ferrel\* attempted to explain some irregularities of oceanic tides, by considering oceans as making stationary oscillations like the seiche in lakes. Recently R. A. Harris†, acting on a similar theory, constructed a co-tidal chart of the world. According to his view, all the water on the globe is divided into several distinct portions, each of which has the period proper to its own stationary oscillation. This point has been subjected to criticism by G. H. Darwin. Harris applied his theory also for the explanation of tidal phenomena in many bays and straits, the standing oscillations of which are forced by tidal waves incident on their mouths. He has considered, however, exclusively the forced oscillation with diurnal and the semi-diurnal periods, and has not considered those oscillations

peculiar to each bay.

Now, according to our view, any bay or gulf, either small or large, may be put into a standing oscillation, if it be excited by the incident waves of a proper period. If the proper period of the bay happens to coincide nearly with one of the tidal components, that component will become more or less prominent, according to the degree of proximity of the proper and the exciting period. In this way, tides of the superior orders or indefinite components arising from meteorological causes, may sometimes become prominent in a bay, though almost insensibly small in the open sea. Moreover, the case may occur in which a solitary wave of wide extent, caused by some disturbances either meteorological or geotectonic, excites the oscillation of a long period proper to a bay. These oscillations in a bay will more or less deform the tidal curve, and cause an anomaly of the tides peculiar to the bay. Believing this view correct, the proper periods as given by our formula were calculated for different bays or gulfs, which are notorious for abnormal range of tide, and also those for which some remarkable irregularities of the tide were observed in the mareograms given in the Report of the Krakatoa eruption. The results of these calculations were found to confirm the above views. Some of the results will be given below.

(i.) Bay of Fundy, Canada.—Near the end of this bay, spring-tides range 15 m., while near its entrance the rise is only 2.5 m. to 3.5 m. For the calculation, the mouth-line was taken from Cape Cod to Cape Sable, and the end of the bay was taken at Port Greville. Then l=460 km. h=141 m;

<sup>\*</sup> Ferrel, "Tidal Researches," Rep. Coast and Geodetic Survey, Washington, 1874.
† R. A. Harris, 'Manual of Tides.'

hence T=13<sup>h</sup>·0. If the mouth-line be taken between Yarmouth and Machias, the calculated period is 11<sup>h</sup>·6. In any case, the proper period of this bay would be very near 12 hours. The abnormally high tide may then in part be explained by the coincidence of the proper period with one of the semi-diurnal tides, though the tidal phase is slightly retarded toward the end of the bay; and therefore the phenomenon cannot be

wholly attributed to the standing oscillation.

(ii.) Bay of Bengal.—Near the mouth of this bay the tidal range is small, being less than half a metre at the southern coast of Ceylon, while in the bay the range is 1-2.7 m., and this increases rapidly near the end of the bay. Since the tidal phase is nearly the same for the greater part of the bay, the principal part of the tide is then probably due to the standing oscillation of it. Taking the mouth-line from the eastern coast of Ceylon to the northern end of Sumatra, and the end of the bay at Akyab in Burma, we obtain l=1500 km. and h=1950 m, which gives  $T=12^{h\cdot0}$ , which coincides with the period of semi-diurnal solar tide.

(iii.) Madura Strait, Java. — Mareograms of Ujong, Sourabaya, and Karang Kleta reproduced in the Krakatoa Report show very marked irregularities of tide in the narrow Strait of Sourabaya, which connects the end of the wide Strait of Madura with the Java Sea. Since the width of the Strait of Sourabaya is extremely small in comparison with that of the Madura Strait, we may consider the latter strait as a reetangular bay, ending at the former strait. The length of the Strait of Madura is about 160 km., and the mean depth of the basin is estimated to be about 30 m., so that the calculated

In order to see whether any long wave corresponding to the calculated period actually exists in records, the mareogram of Karang Kleta was analysed by means of the tiderectifier\*, and an evident trace of waves with the mean period of 8<sup>h</sup>·0 was found. The exciting cause of this wave may be the compound tide usually denoted by MK, the period of which is about 8<sup>h</sup>·2, which nearly coincides with

the proper period of the Madura Strait.

period becomes 8h.8.

(iv.) Port Adelaide, Australia.—A mareogram of this Port, given in the Krakatoa Report, shows a remarkable variety of diurnal inequalities on successive days. On eliminating the principal parts of diurnal tides, the resulting curve shows an

<sup>\*</sup> Terada, Publications of Earthquake Investigation Committee in Foreign Languages, xviii. 1904.

apparent beat of semi-diurnal tides. The period of the characteristic component, which forms a beat with the usual semi-diurnal tide, is about  $10^{\text{h}\cdot 9}$ , as estimated from the rectified curve. It is probably to be attributed to the standing oscillation of the St. Vincent Gulf. Taking the mouth-line from Troubridge Point to Cape Jevis, and the end of the gulf at Wakefield, we obtain l=140 km., and the estimated mean depth is 21.5 m. Hence  $T=10^{\text{h}\cdot 8}$ , which coincides very well

with the observed period.

(v.) Port Phillip, Australia.—Mareogram of Williamstown given in the above quoted Report shows some irregularities of tide, which suggests the existence of very long undulations peculiar to the bay. The curve was rectified and a period of  $8^h$ :3 was detected. Now the period of seiches in this nearly enclosed basin can by no means become so long as  $8^h$ , unless the mean depth of the Port be less than one metre. This period is probably due to the undulation of the whole basin with its narrow neck communicating with the open sea. For the calculation of the period corresponding to this mode, the necessary data were estimated from the chart given in Harris's Report:  $S=13.7\times10^8$  m.², l=2.95 km., b=4.08 km., h=18.4 m. and L=200 km. The period calculated from these data is  $8^h$ :39 by formula (5), § 4, which almost coincides with the observed period.

Besides the above enumerated examples, there are many bays, or straits, the forms of which seem favourable for their own standing oscillation of long periods, and in which the ranges of tides are comparatively large. The periods of these

oscillations were estimated as follows:-

Bay or Strait.	T in hours.
Adriatic Sea	15
Mozambique Channel	7
Bristol Bay, Alaska	15 and $28$
Hecate Strait, British Columbia	7
Hudson Strait, Canada	11
Bristol Channel, England	5
Gulf of St. Malo, France	7

As we have no tidal records of these bays and channels at hand, discussion must be omitted. We conclude this section

by calling the attention of oceanographers to the proper oscillation of large bays.

In conclusion we wish to express our best thanks to Professor H. Nagaoka, under whose supervision the present work has been carried out. Equal thanks are due to Professor F. Omori, who favoured us with many records of sea-waves. Lastly, our cordial thanks are due to Dr. Y. Yoshida, Dr. N. Watanabe, Dr. S. Iwamoto, Dr. Y. Inouye, Dr. J. Fukuda, and Dr. Hirata, who have been zealous cooperators in the course of the observations.

IX. On the Joule-Kelvin Inversion Temperature, and Olszewski's Experiment. By J. D. Hamilton Dickson, M.A., Fellow of Peterhouse, Cambridge; F.R.S.E.\*

#### [Plate VIII.]

THE condensation of gases and the means of reaching low temperatures have, within the last dozen years, brought into prominence what is called the Joule-Kelvin inversion-temperature. Whether Mayer's hypothesis would be established as a fact, led to Joule's experiments on the expansion of a gas at high pressure. These experiments seemed to establish this hypothesis as true; but the more ingenious method of experimenting suggested by Kelvin, in which sudden expansion through a small aperture from a high pressure to a low one was replaced by continued expansion through a porous plug between two pressures differing but little from each other, brought out the fact that in general such expansions produced cooling, and thus disproved Mayer's hypothesis.

This result was at first found to be true of all gases; but further examination of hydrogen showed that heating was experienced in its case. The theory of the porous-plug experiment was given at the time by Kelvin, and the prime use made of it then was to determine how far "absolute temperature" differed from temperature given by an airthermometer. The most careful precautions were taken, by means of concomitant correction experiments, to determine exactly the conditions of the porous-plug experiment; and it may be said today, that after a lapse of nearly 60 years

no improvement has been made in them.

<sup>\*</sup> Communicated by the Author.

Kelvin's formula, governed by the conditions of the Joule-Kelvin experiment, is, in the usual notation,

$$Q = \int_{v}^{v'} p \, dv + pv - p'v' - t \int_{v}^{v'} \frac{dp}{dt} \, dv, \quad . \quad . \quad (1)$$

where Q is the quantity of heat lost by the gas through traversing the porous plug from a higher to a lower pressure. There are two other forms in which this may be written, namely,

$$Q = \int_{p}^{p'} \left( t \frac{dv}{dt} - t \right) dp, \quad . \quad . \quad (2)$$

and

$$Q = (U' + p'v') - (U + pv), (3)$$

each being, on occasion, more suitable than the other two for a particular discussion. In the practical application of the results of their experiments, Joule and Kelvin employed a formula sent them by Rankine\*, which accorded with their experimental results, showing that the fall of temperature varied inversely as the square of the absolute temperature. After this followed Andrews's epoch-making experiments on the continuity of state; and a little later, van der Waals's Thesis, which, leaving the Boyle-Charles laws as a first approximation to the equation of state of a gas, gave distinct and permanent advance to our theoretical knowledge of the properties of a gas by means of the well-known equation

$$\left(p + \frac{a}{\overline{v^2}}\right)(v - b) = Rt. \quad . \quad . \quad . \quad (4)$$

In his thesis he discussed Andrews's experiments, and showed that this equation produced the form of the isothermal which James Thomson had suggested as probable. He also discussed the Joule-Kelvin porous-plug experiment, and by means of the same equation deduced for it a theoretical relation, when the pressure is not too high, which he expressed (in his notation) by the equation †

$$424 c(t_1 - t) = \frac{10334}{1 \cdot 293 d_0} \left(\frac{2a}{1 + \alpha t} - b\right) \frac{p_1 - p}{p_0} . \quad . \quad . \quad (5)$$

The accuracy of this equation for air was remarkable; for, by calculation, he found that the fall of temperature per atmosphere was 0.265, while the average of seven results quoted from Joule and Kelvin's work, and ranging from

† English translation, p. 444.

<sup>\*</sup> Kelvin, Collected Papers, vol. i. pp. 376, 391.

·2429 to ·2881, was ·2593. There was some discrepancy in a similar calculation for carbonic acid, but not enough to reject the claim that his theory was substantiated by its coincidence with experiment. Shortly after van der Waals's thesis was published Clausius proposed a modification of it in two directions, the principal one being that the molecular attraction constant should vary inversely as the temperature. On this assumption, for small pressures, we get the relation

$$JC_{p}\frac{dt}{dp} = \frac{3a}{Rt^{2}} - b; \qquad (6)$$

thus introducing the inverse square of the temperature, in accordance with Joule and Kelvin's experiments and

Rankine's theoretical equation.

It will not be a matter of surprise that two formulæ so different should both approximately satisfy the experimental results, when we consider that on the p, t plane these results would be plotted within a range of some 4 or 5 atmospheres and some 80 degrees of temperature. Two such curves, threading their way for the short distance necessary among the experimental points plotted on this

area, would practically coincide.

Great developments of the experimental methods of Cailletet and Pictet have been made in the last 25 years, notably by Dewar, Olszewski, and Linde. To the first of these, by the invention of the vacuum-jacketed flask and by his subsequent masterly use of it, we owe the production of liquid oxygen and hydrogen in bulk under atmospheric pressure, and also solid oxygen, air, and hydrogen, thus reaching the lowest temperature yet attained; while, on the other hand, the last-named physicist has devised means to produce liquid air and oxygen commercially. Olszewski, in particular, has studied the lowering of temperature by expansion and has, for his researches, modified in some important points both the Joule and the Joule-Kelvin experiments. In the Olszewski experiment a finite time is occupied in the release of the gas under pressure, thus differing from the method followed by Joule. There is also a departure from the Joule-Thomson porous-plug experiment in employing a great difference of pressures, and (at least as far as can be made out from published papers) in restoring the small aperture in place of the porous plug. The questions arise: Is the theory of the Olszewski experiment the same as that of the Joule-Kelvin experiment? If not, what is the theory? And with these questions there

arises another, What is meant by the Joule-Kelvin inversion-

temperature?

For some time the idea has held ground that by merely dealing with the Joule-Kelvin experiment at higher or lower temperature, one temperature would be found at which the escaping gas would show neither heating nor cooling. is correct provided the temperature does not exceed a certain But the further extension has been made, that the same would still hold true if a great difference of pressures was employed. Here, however, the conditions of the Joule-Kelvin experiment may be infringed, and without formal proof we are not at liberty to make this assumption. properties of a gas depend in general on two of the three quantities, pressure, volume, and temperature, because we have an equation of state connecting the three. If a certain property depends on the alteration of one of these quantities only, some condition must in general have been assumed, even although tacitly. In the first idea of the inversiontemperature; the tacit assumption was (at least) that the difference of pressures was small; perhaps there was also the idea that the pressures themselves were small. But in any case, Kelvin's formula fully provided for any pressures so long as the conditions of the experiment were maintained. The Boyle-Charles laws were originally employed in the numerical reduction of the Joule-Kelvin observations; later, a formula due to Rankine was used; today we may employ van der Waals's relation as a step nearer the actual condition of a gas.

I shall use equation (1) for my purpose, and substitute in it from equation (4), noting that in general undashed letters refer to the initial state (the state of higher pressure) and

dashed letters to the final state. Thus we get

$$Q = Rt \left( \frac{v'}{v'-b} - \frac{v}{v-b} \right) - 2a \left( \frac{1}{v'} - \frac{1}{v} \right), \quad . \quad . \quad (7)$$

whence, on putting Q=0, the inversion-temperature  $t_i$  is given by

$$Rt_i = \frac{2a}{b} \left( 1 - \frac{b}{v} \right) \left( 1 - \frac{b}{v'} \right), \quad . \quad . \quad . \quad . \quad (8)$$

or, if  $t_c$  is the critical temperature,

$$t_i = \frac{27}{4} t_c \left( 1 - \frac{b}{v} \right) \left( 1 - \frac{b}{v'} \right). \tag{9}$$

Phil. Mag. S. 6. Vol. 15. No. 85. Jan. 1908.

If the initial pressure is great while the final one is small, we may neglect the fraction b/v', and take the simpler form of the equation,

 $t_i = \frac{27}{4} t_c \left( 1 - \frac{b}{v} \right);$  (10)

and if both pressures are small, we get the limiting equation

$$t_i = \frac{27}{4}t_c$$
. (11)

To show the differences between these equations, let us take Olszewski's \* highest values for air, namely, p=160,  $t_i=532^{\circ}$  abs. Inserting these two values in van der Waals's equation,

 $\left(p + \frac{1682}{v^2}\right)(v - 1.528) = 2.835t, \dots$  (12)

in which the values of a, b, R for one atmosphere as unit pressure, and a cubic centimetre as unit volume, have been deduced from the values a=0.037, b=0.026 given by him † for the pressure of a metre of mercury as unit pressure, and the volume of the gas at 0° C. and under this pressure as unit volume, we find the value of v for one gram of air to be approximately 10.07 c.c. Hence equation (9) gives  $t_c=93^{\circ}$ , while the limiting equation (11) would give 78°8. Neither of these values is near the true value, 133°; but we see that the effect of the value of b, although it is only about  $1\frac{1}{2}$  c.c. in comparison with some 773 c.c. as the specific volume of air, when associated with a certain high pressure, is to give values for the critical temperature which differ in the ratio of 6 to 7. Otherwise, equations (9) (for two nearly equal pressures at 160 atmos.) (10), (11) make the ratio of the temperature of inversion to the critical temperature 4.86, 5.72, and 6.75 respectively. From van der Waals's constants for air, and his own formula, equation (5), the temperature of inversion is about  $770^{\circ}$  abs., or  $5.84 \times 133^{\circ}$ ,  $133^{\circ}$ being the critical temperature quoted by Olszewski, Linde, and Berthelot. It may be noted that these temperatures increase as the initial pressures diminish.

In 1887 E. Natanson ‡, by an elaborate series of experiments on carbonic acid, conducted on Joule and Kelvin's lines, showed that the cooling of this gas on passing the porous plug was not independent of the pressure.

In 1898 Witkowski, after a most careful experimental

<sup>\*</sup> Phil. Mag. June 1907, vol. xiii. p. 723.

<sup>†</sup> English translation, p. 400. ‡ Wied. *Ann.* xxxi. p. 518 (1887).

study of the properties of air, published a memoir \* on the behaviour of this gas in the Joule-Kelvin experiment; but, instead of basing his investigation on any theoretical equation, he employed his own experimental results, involving them in the thermodynamic equation by the method of quadratures. Taking U for the internal energy, he calculated the values of the function U + pv for the pressures and temperatures within the range of his experiments. With these he plotted a series of curves of constant pressure, the coordinates being temperature and the excess of the function U+pv for pressure p above its value for one atmosphere. From these curves he constructed curves for constant values of  $U + \rho v$ , with pressure and temperature as coordinates. The range of these curves being from about 130° to 273° (abs.), and therefore not including the (so-called) inversion-temperature, he pointed out that it was possible, if they had extended farther, to have found the slope of the U+pv curves changing sign, and hence to have determined this temperature. Thus to Witkowski is due the proof of the fact, based on accurate experiment, that for the determination of any such temperature it is necessary to take the pressure also into consideration.

In 1906, after the publication of Olszewski's results on the release of hydrogen from high pressure, Porter† examined the question, using also the function U+pv. He plotted curves of constant pressure (such curves may be called isopiestics), using as coordinates the temperature and the variable part, independent of temperature, of the indefinite function U+pv. But instead of employing experimental results, he used various theoretical equations, and in particular van der Waals's equation of state. Equation (7) may

be written

$$Q = \left(\frac{Rtv'}{v'-b} - \frac{2a}{v'}\right) - \left(\frac{Rtv}{v-b} - \frac{2a}{v}\right),$$
or, by (4), 
$$Q = \left(p'v' - \frac{a}{v'}\right) - \left(pv - \frac{a}{v}\right);$$
(13)

and we have also

$$U + pv = \phi(t) - \frac{a}{v} + pv,$$
 . . . (14)

where  $\phi(t)$  is an unknown function of the temperature. Porter took  $pv - \frac{a}{v}$  for his abscissa (the *minus* appears as

<sup>\*</sup> Anzeiger d. Akad. d. Wiss. in Krakau, 1898, pp. 282-295.

plus in his paper) and temperature for the ordinate, both in reduced coordinates.

In discussing the problem we may proceed along two lines, and it will be instructive to follow both. We may eliminate v and v' from equation (8) by means of an equation (4) for each; or, we may examine the properties of the isopiestics plotted to the reduced values of  $pv - \frac{a}{v}$  and t as coordinates. There is important information to be got from both methods; meanwhile, equations (13) and (14) show that the two methods are equivalent.

The function U+pv being of the nature of a potential, I shall, in what follows, use this name for it; and in this connexion isopotential curves will also be employed. We have to find the equation connecting the inversion-temperature with the initial and final pressures. As the rest of the investigation deals only with this temperature, we may drop

the suffix i, and understand that t refers only to it.

The result of eliminating v and v' between the equations

$$Rt = \frac{2a}{b} \left( 1 - \frac{b}{v} \right) \left( 1 - \frac{b}{v'} \right), \qquad (8)$$

$$\left(p + \frac{a}{v^2}\right)(v - b) = Rt, \quad . \quad . \quad . \quad (4)$$

$$\left(p' + \frac{a}{v'^2}\right)(v' - b) = Rt, \quad . \quad . \quad . \quad (4')$$

may be written in the simple form

$$(P + \pi + \frac{1}{2}r + u)^2 = 8\pi u,$$
 (15)

where

re
$$P = \frac{1}{2}(p+p'), \quad \pi = \frac{a}{b^2}, \quad r = \frac{Rt}{b}, \quad \delta = p - p',$$
and
$$u = \frac{\sqrt{\delta^2 + r^2} + r}{2},$$
(16)

If the pressures differ only slightly, as in the Joule-Kelvin experiment, we may in the limit take them as equal, and consequently put  $\delta = 0$ , P = p, u = r, and equation (15) becomes

$$(p+\pi+\frac{3}{2}r)^2=8\pi r$$
. . . . (17)

This equation agrees with equation (10) in Dewar's paper \*

<sup>\*</sup> Proc. Roy. Soc. March 1904, vol. lxxiii. p. 260.

on "Physical Constants at Low Temperatures," namely,

$$t = 3t_c \left(1 + \frac{1}{2} \sqrt{1 - \frac{p}{9p_c}}\right)^2$$
.

We can also verify this result directly. For putting v=v' in equation (8), it becomes

$$Rt = \frac{2a}{b} \left( \frac{v - b}{v} \right)^2, \quad . \quad . \quad . \quad (18)$$

whence, if  $\xi^2 = \frac{bRt}{2a}$ , van der Waals's equation (4) becomes

$$p + \frac{a}{b^2}(1-\zeta)^2 = \operatorname{Rt} \frac{1-\zeta}{b\zeta} = 2\frac{a}{b^2}\zeta(1-\zeta),$$

or

$$p + \frac{a}{b^2} + \frac{3}{2} \frac{Rt}{b} = \sqrt{8 \frac{a}{b^2} \frac{Rt}{b}},$$

which is equation (17). But equation (15) is not in a suitable form for the determination of t from given values of p and p'. Expanding, and arranging it in powers of r, it takes the form

$$9r^{4} + 16 (\pi + 3P)r^{2} - 2\{4(\pi + P)(5\pi - 11P) + 3\delta^{2}\}r^{2} - 16 \{4(\pi + P)^{2}(\pi - P) - (5\pi - P)\delta^{2}\}r + 16(\pi + P)^{4} - 8\{2(3\pi - P)^{2} - (\pi + P)^{2}\}\delta^{2} + \delta^{4} = 0; (19)$$

which shows at once that the inversion-temperature is a complicated function of the initial and final pressures. It is interesting, however, to note that it depends, not explicitly upon them, but only upon their difference  $\delta$ , and their arithmetic mean P. Further, since  $\delta$  occurs only under the square and the fourth power, the phenomenon, but for other reasons, would be reversible. Putting  $\delta = 0$ , we ought to recover the equation for the Joule-Kelvin experiment; and this is the case, for the terms without  $\delta$  are

$$9r^4 + 16(\pi + 3P)r^3 - 8(\pi + P)(5\pi - 11P)r^2 - 64(\pi + P)^2(\pi - P)r + 16(\pi + P)^4,$$

which can be written as the product

$${9r^2-4(5\pi-3P)r+4(\pi+P)^2}(\pi+P+\frac{1}{2}r)^2$$
, (20)

the first of whose factors equated to zero, and with p written for P, is equation (17). The second factor cannot vanish, since each of its terms is positive.

We can now answer the question, What is meant by a Joule-Kelvin inversion-temperature? Gas is allowed to expand through a porous plug from a high pressure of any

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magnitude to a lower pressure of any magnitude subject to certain conditions, namely, it must enter and leave the neighbourhood of the plug at the same temperature; some considerable time must elapse between the starting of the experiment and the commencement of observations so that the flow of gas may be steady both as regards pressure and temperature; the gas must leave the plug with kinetic energy differing so little from that with which it approaches the plug that this difference may be neglected; then, the temperature in question is an inversion-temperature for the gas concerned and the pressures employed.

For the discussion of the general question it is convenient to express equation (19) in reduced coordinates. Let  $\alpha$ ,  $\alpha'$ 

be reduced pressures, and put

$$\sigma = \frac{\alpha + \alpha'}{54}, \quad \epsilon = \frac{\alpha - \alpha'}{27}, \quad r = \beta \frac{\alpha}{b^2}, \quad . \quad . \quad . \quad (21)$$

the equation then becomes homogeneous and of the fourth power in  $a/b^2$ . On dividing this factor out, it takes the form

$$\begin{split} 9\beta^4 + 16(1+3\sigma)\beta^3 - 2\{4(1+\sigma)(5-11\sigma) + 3\epsilon^2\}\beta^2 \\ - 16\{4(1+\sigma)^2(1-\sigma) - (5-\sigma)\epsilon^2\}\beta \\ + 16(1+\sigma)^4 - 8\{2(3-\sigma)^2 - (1+\sigma)^2\}\epsilon^2 + \epsilon^4 = 0, \quad (22) \end{split}$$

whence the reduced temperature corresponding to any pair of pressures  $\alpha$ ,  $\alpha'$  is  $\frac{27}{8}\beta$ .

As numerical examples of equation (22), I have taken the case of a gas with a critical pressure of 40 atmospheres, and have supposed expansions, on the Joule-Kelvin process of experiment, to take place from 160, 120, 80 and 40 atmospheres in each case to one atmosphere. Thus the values of  $\alpha$  are 4, 3, 2, 1 respectively, and that of  $\alpha'$  is  $\frac{1}{40}$ . Linde and Berthelot quote 39 atmospheres as the critical pressure of air, so that the following results will approximate to those for air, on the suppositions made.

The four equations are:—

for 
$$\alpha = 4$$
,  $\alpha' = \frac{1}{40}$ ,  
 $9\beta^4 + 19 \cdot 575\beta^3 - 36 \cdot 06\beta^2 - 66 \cdot 66\beta + 18 \cdot 56 = 0$ ;  
for  $\alpha = 3$ ,  $\alpha' = \frac{1}{40}$ ,  
 $9\beta^4 + 18 \cdot 685\beta^3 - 37 \cdot 10\beta^2 - 66 \cdot 37\frac{1}{2}\beta + 18 \cdot 31 = 0$ ;  
for  $\alpha = 2$ ,  $\alpha' = \frac{1}{40}$ ,  
 $9\beta^4 + 17 \cdot 795\beta^3 - 38 \cdot 10\beta^2 - 65 \cdot 86\beta + 17 \cdot 82 = 0$ ;  
for  $\alpha = 1$ ,  $\alpha' = \frac{1}{40}$ ,  
 $9\beta^4 + 16 \cdot 908\beta^2 - 39 \cdot 05\frac{1}{2}\beta^2 - 65 \cdot 06\beta + 17 \cdot 07 = 0$ .

Of these the required roots are

$$1.845$$
,  $1.886$ ,  $1.923$ ,  $1.960\frac{1}{2}$ 

respectively: hence, on the hypothesis of van der Waals's equation of state, a porous-plug experiment conducted with the limitations of the Joule-Kelvin experiment, gives an increasing temperature of inversion for a falling initial pressure, the expansion taking place against a pressure of one atmosphere. The following Table collects these results:—

a,	β.	Reduced	Initial	Inversio	n-temp.	Olszewski for	
		temp.	pressure.	Abs.	Cent.	Abs.	Cent.
4	1.845	6:227	160 atm.	828.4	555.4	$53\overset{\circ}{2}$	$25\mathring{9}$
3	1.886	6.366	120 ,,	846.8	573.8		•••
2	1.923	6.492	80 ,,	863.4	590.4	513	240
1	$1.960\frac{1}{2}$	6.618	40 ,,	880:3	607:3	471	198

and as air has a critical pressure of nearly 40 atmospheres, I have assumed it (approximately) as being treated by these equations, and have therefore used its critical temperature of 133° abs. to get the temperatures in the fifth and sixth columns of the table. The seventh and eighth columns contain temperatures from Olszewski's published numbers\*. Hence it would appear that the Olszewski experiment differs fundamentally from that of Joule and Kelvin, for his results show a falling inversion-temperature with a falling initial pressure, which is contrary to the results of the theory of the Joule-Kelvin experiment.

The conclusion thus reached will be verified by the second mode of consideration of the problem, namely, by direct examination of the isopiestics drawn on the temperature-potential plane, and based on van der Waals's equation. Taking x to represent potential, and y to represent temperature, in reduced coordinates, we have

$$9x = \alpha \phi - \frac{3}{\phi}$$
,  $8y = (3\phi - 1)(\alpha + \frac{3}{\phi^2})$ , . . (24)

 $\alpha$  and  $\phi$  being reduced pressures and volumes respectively.

<sup>\*</sup> Phil. Mag. June 1907, vol. xiii. p. 723.

or

It will be necessary to get the equations to these isopiestics Eliminating  $\phi$  from (24), after a few steps we have

$$729x^{3} - 216x^{2}y + (729 - 27\alpha)x^{2} - 64y^{2} + 108\alpha x - 32\alpha y + (108\alpha - 4\alpha^{2}) = 0. \quad . \quad (25)$$

We shall also require the envelope of these isopiestics; its equation, following the usual process, is immediately

$$16(729x^{3} - 216x^{2}y + 729x^{2} - 64y^{2}) + (27x^{2} - 108x + 32y - 108)^{2} = 0$$

$$(x+2)^{2} \left\{ (x+2)^{2} - \frac{64}{27}y \right\} = 0 \qquad (26)$$

showing that the envelope is a parabola. This envelope is the locus of points representing an expansion between pressures differing only infinitesimally in a Joule-Kelvin experiment, and (for the present) appears to be independent of the magnitude of the pressures, but we shall see later that only a finite portion of the curve is involved in the question, and also a limited range of pressures. We ought to arrive at the same result from Porter's equations (pp. 555, 556 of his paper). Writing them in the present notation they are

$$y = \frac{3}{4} \left( 3 - \frac{1}{\phi} \right)$$
, and  $x = \frac{\alpha \phi}{9} - \frac{1}{3\phi} = 2 - \frac{4}{\phi}$ ,  $y = \left( \frac{3}{4} \right)^3 (x+2)^2$ ,

whence

thus verifying equation (26).

These isopiestics and their relation to the envelope are shown in fig. 1, Pl. VIII. The zero-isopiestic consists of the straight line  $O\omega$ , and the parabolic arc  $O\psi$ , whose equations are

$$27x - 8y = 0$$
 . . . . . . . . . . . (27)

and

$$27x^2 + 27x + 8y = 0$$
. . . . (28)

The envelope VMLN is touched by this isopiestic twice, namely, at the points M, N. As  $\alpha$  increases from zero the successive isopiestics each touch the envelope at two points, the one leaving M, the other N, and approaching each other towards L. These points of contact are given, for the  $\alpha$ -isopiestic, by the equations

$$x+2=\pm \frac{4}{9}(u\pm 6), \quad y=\frac{(u\pm 6)^2}{12}, \quad . \quad . \quad (29)$$

where  $u^2 = 9 - \alpha$ . Hence we see again that  $\alpha$  cannot exceed 9,

and that the 9-isopiestic touches the envelope in two coincident points at L, which we may call the final point of contact, its coordinates being x=2/3, y=3. Thus the part of the parabola which constitutes the envelope is contained between M and N, and deals only with pressures within the range  $\alpha=0...9$ . Further, a Joule-Kelvin experiment, in which the pressures are nearly equal, and as governed by van der Waals's equation, cannot involve pressures higher than nine times the critical pressure. This limitation has been noticed by Dewar, Berthelot, and others; and it agrees with Porter's full-line curve (p. 556 of his paper), for its equation may be put in the form

$$(\xi + 12\eta - 45)^2 = 144(9 - \xi), \quad . \quad . \quad (30)$$

where  $\xi$  is reduced pressure, and  $\eta$  is reduced temperature, and real solutions of this equation require  $\xi$  not to exceed 9. Equation (30) is that of a parabola, cutting the axis of temperature at the reduced temperatures 3/4 and 27/4, the latter result agreeing with equation (11).

From equations (29) we get the positions of the points M, N, namely, M is  $(-\frac{2}{3}, \frac{3}{4})$ , N is  $(2, 6\frac{3}{4})$ . The following Table will help to show how these points of contact follow each other,  $(x_1, y_1)$  being the lower, and  $(x_2, y_2)$  the higher point of contact for any one isopiestic. For values of  $\alpha$ 

a.	$x_{1}$ .	$y_1$ .	$x_2$ .	$y_2$ .
0	-0.67	0.75	2.00	6.75
1	-0.59	0.84	1.92	6.49
3	•••			
	•••			
4	***	•••		• • • •
5	-0.22	1.33	1.56	5.33
$6\frac{3}{4}$	0.	1.69	1.33	4.69
7	•••	•••		
8	0.22	2.08	1.11	4.08
9		0.67	y = 3.00.	

greater than 9, no isopiestic touches the envelope; that is, there is no inversion-point for a Joule-Kelvin experiment, the pressures differing by only a small amount, when these pressures exceed nine times the critical pressure. But there are inversion-points for finite differences of pressure within certain limits, as we shall find later.

If we seek for the general circumstances in which a given temperature may be an inversion-temperature, we find that

for such a temperature two isopiestics must intersect. I distinguish between an inversion-point and an inversiontemperature; and it will be convenient to refer to the two isopiestics passing through any inversion-point as the higher and the lower according as the corresponding  $\alpha$  has a greater or less value. An examination of fig. 1 will lead to the following conclusions, which have been verified by calculation. All points of intersection of any two isopiestics lie within the curvilinear triangle MONLM; hence inversion points only exist within, or on the contour, of this triangle. The highest isopiestic which can take part in determining an inversion-temperature is  $\alpha = 27$ , for this isopiestic cuts the triangle only at the point O. Any isopiestic between this and  $\alpha = 9$  may be the higher of the two isopiestics of any inversion-point. Any isopiestic from  $\alpha = 9$  to  $\alpha = 0$ , inclusive, may be the lower of the two required; and no isopiestic above  $\alpha = 9$  can be the lower one. Every lower isopiestic (i. e. one whose  $\alpha < 9$ ) can only have associated with it as the higher isopiestic, one from a limited range of isopiestics extending from itself to a particular value of a, depending upon the lower isopiestic, and less than 27. Thus, in fig. 1, it is easy to see that the range for  $\alpha=1$  extends to about 22—the last being that isopiestic which touches  $\alpha=1$ and lies not quite half-way from 20 to 25; similarly for  $\alpha = 5$ , the range gets to about 14. No temperature can be an inversion-temperature which exceeds 63 times the critical temperature. For every temperature below this value, any point on the horizontal line representing that temperature, and lying within the curvilinear triangle, gives a pair of pressures which have this temperature for inversion-temperature. Thus in order that three times the critical temperature may be an inversion-temperature, we may begin with a pressure of about 21½ times the critical pressure and expand into a vacuum; or we may use an initial pressure of 20 times the critical pressure and expand down to the critical pressure; or finally we may employ two nearly equal pressures about 9 times the critical pressure.

The equation (25) for the isopiestics may be regarded from other points of view, each of which will, on occasion, be preferable, as helping us to see more clearly the limitations of the question. It expresses a relation between x, y, and  $\alpha$ —potential, temperature, and pressure. By making  $\alpha$  constant we have already got the equations of the isopiestics in the temperature-potential plane. If we make  $\alpha$  constant, we shall have the equations of the isopotentials in the temperature-pressure plane; and if we make  $\alpha$  constant, we shall have the

equations of the inversion-isothermals in the potential-pressure plane. The isopotentials correspond to Witkowski's\* second (derived) curves. Equation (25) rewritten in a more suitable form for an isopotential is

 $(8y+2\alpha)^2+216x^2y+27(x^2-4x-4)\alpha-729x^2(x+1)=0$ , (31) in which x is to be given any constant value. For different constant values of x, this is the equation of a series of parabolas whose axes are parallel and make with the axis of temperature an acute angle of  $14^\circ$  2' [the scales in fig. 2 reduce this angle to  $1^\circ$  26']. In fig. 2 these parabolas are shown; they have there been derived directly from measurements made on fig. 1, and not by means of equation (31). The curve ABCD is the curve corresponding to the envelope VMLN in fig. 1. Like it, it extends from y=75 to y=6.75, the greatest pressure associated with any point on it being 9, when y=3 (corresponding to the point L). This curve is the parabola whose equation has already been given in (30), and of which another useful form is

$$(12y + \alpha + 27)^2 = 1728y$$
; . . . (32)

it touches the axis of pressure at the negative pressure -27. The axis of temperature in fig. 2 corresponds to the zero-isopiestic in fig. 1. The advantage of the new figure is now apparent. The inversion-points in fig. 1 were all confined within a rather confusing curvilinear triangle; they are now contained within the more open curvilinear quadrilateral BDEB' bounded by the portions of the axes BD, B'E, and the parabolas BB', DE whose equations are, respectively.

$$(4y+\alpha)^2 + 24y - 6\alpha - 27 = 0 . . (33)$$

and

$$16y^2 + 27\alpha - 729 = 0$$
. (34)

The circumstances in which inversion will take place are now to be found from a line of constant temperature. Thus if we look along the line for which y=2 we see that inversion will take place for a gas expanding from an initial pressure of about  $24\frac{1}{2}$  times the critical pressure into a vacuum, the potential being '6; or between pressures 22 and 1, the potential being '5; or between pressures 15 and  $3\frac{3}{4}$ ; the potential being '3; or finally between two nearly equal pressures of about 8 times the critical pressure. Witkowski's isopotentials lie within the rectangle bounded by y=0.9, y=2.1, and  $\alpha=0$ ,  $\alpha=4$ .

Instead of representing the isopotentials we may obtain perhaps a better display of the circumstances of inversion by means of the inversion-isothermals,—curves of constant inversion-temperature drawn with potential and pressure as coordinates. These are given in fig. 3, and have been drawn from readings taken directly from fig. 2. If we want to arrange for 1.4 times the critical temperature as an inversion temperature, we may expand the gas from about 25 times the critical pressure down to a vacuum; or from about  $19\frac{1}{2}$  down to about  $1\frac{1}{4}$  times the critical pressure; or from  $13\frac{1}{2}$  to  $2\frac{1}{2}$ ; or from 10 to  $3\frac{3}{4}$ ; or, finally, a Joule-Kelvin experiment may be made for this temperature as an inversion-temperature if we expand the gas from a little above to a little below  $5\frac{3}{4}$  times the critical pressure. Joule-Kelvin experiments with small differences between the two pressures are represented by points on the parabolic are FGH...KJ, whose equation is

$$9(3x-2)^2=16(9-\alpha)$$
. (35)

The area of inversion is here again a curvilinear quadrilateral. It is bounded by the axis of x, and the isopotential  $x = -\dot{6}$ , by the zero-isothermal, and by a parabolic arc, part of which is the curve ST whose equation is

$$27x^2 + 4\alpha = 108.$$
 . . . . . (36)

These inversion-isothermals will afford the means of clearly testing the reduction of Olszewski's observations made recently by Porter. The basis of his calculation is that from Olszewski's experiments the inversion-temperature is \* "about 5.8 times the critical temperature." Putting y=5.8 in equation (25), the quadratic for  $\alpha$  is

$$4\alpha^{2} + (27x^{2} - 108x + 77.6)\alpha - (729x^{3} - 523.8x^{2} - 2152.96) = 0,$$

$$...$$
(37)

from which the following Table has been calculated.

x.	<i>a</i> <sub>1</sub> .	a <sub>2</sub> .
1.70785	3.5	119
1.7105	5.28	1.76
1.715	6.41	0.64
1.7185	7.065	. 0
1.725	8.03	-0.93
1.750	10.69	-3.51
1.8	14.33	-7.00
1.9	19.68	-12.15
2.0	24.06	-16.46

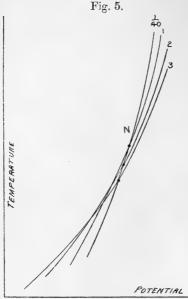
<sup>\*</sup> Loc. cit. p. 563.

In fig. 4 (a continuation of fig. 3, but with the scale of potential doubled, to bring the circumstances more clearly in evidence) the inversion-isothermal is drawn from this table. The available portion PQR of this isothermal lies to the left of the vertical through P, where it cuts the axis of potential. The highest available pressure for this isothermal is 7.065 times the critical pressure, and the associated low pressure must be that of a vacuum. Porter notes \* that "in Olszewski's experiment with hydrogen the initial pressure was eight times the critical pressure, and the final pressure was atmospheric, i. e. roughly  $\frac{1}{20}$  the critical value." These circumstances do not coincide with the present more complete determination of the point in question based on van der Waals's theory, which Porter also employed; nor, in fact, with the data given by Olszewski. In the paper communicated to the Philosophical Magazine "by the author," Olszewski states † that he began with "about 170 atmospheres" and got "considerable" cooling at "about -190° ": that he next employed 150 atmospheres at -103° and again got a fall of temperature; that he only succeeded finally in getting constancy of temperature when the initial pressures during a series of 25 experiments "fell from 117 to 110 atmospheres." If then we still take 20 atmospheres as the critical pressure, these pressures correspond to values of a lying between 5.85 and 5.2 (and not to  $\alpha = 8$ ), and the 5.8 inversion-isothermal shows that the final pressures (reading from the curve) would require to be about 1.2 to 1.9 times the critical, or 24 to 38 atmospheres. values which cannot be considered as approximations to the experimental value of one atmosphere. If we take a lower value of the critical pressure (in accordance with Olszewski's later experiments), say 15 atmospheres, then a ranges from 7.8 to 7.2; but the verticals through these points cut the isothermal in the region of negative pressure, which is inadmissible. To put the critical pressure lower would only enhance this divergence from admissibility. The conclusion seems clear, therefore, that on the data, and employing van der Waals's equation of state, the physical nature of Olszewski's experiment has still to be determined.

In this conclusion I believe I am confirmed by the recent observations published by Olszewski‡ on Air and Nitrogen. These experiments show a diminishing temperature of inversion with a falling initial pressure, the final pressure in each case being one atmosphere. For an experiment following exactly the conditions of the Joule-Kelvin porous-plug

<sup>\*</sup> Loc. cit. p. 563. † Phil. Mag. May 1902, vol. iii. p. 539. † Phil. Mag. June 1907, vol. xiii. p. 723.

experiment, the constancy of the potential function U+pv is accepted. The inversion-points concerned are (fig. 1) the points of intersection of the isopiestic  $\alpha = \frac{1}{40}$  (approximating to the case of air) with isopiestics ranging from  $\alpha = 0.5$  to  $\alpha = 4.0$ . These points lie near N\*, within the sharp apex of the curvilinear triangle. A somewhat expanded portion of this part of fig. 1 is given in fig. 5, which shows the intersections of the isopiestics  $\alpha = 1, 2, 3$  with  $\alpha = \frac{1}{40}$ . These



four isopiestics touch the envelope at increasing distances from N (the point of contact of the zero-isopiestic, at the reduced temperature 27/4), and it is clear that the points of section of  $\alpha = \frac{1}{10}$  by  $\alpha = 1$ , 2, 3 must be at successively lower points in the figure; that is, at successively lower temperatures. In other words, as  $\alpha$  increases in this neighbourhood, the lower pressure being always constant, the successive inversion-temperatures must fall. This verifies the result of the direct calculation earlier in the paper. In fact the locus of actual Joule-Kelvin inversion-points in this neighbourhood

<sup>\*</sup> These isopiestics intersect again within the inversion triangle near M, but the temperatures at M are only slightly above the boiling-point, and differ greatly from those in the Olszewski experiments. It may be noted that this is an inversion region deserving attention. All lower isopiestics, for which  $\alpha < 1$ , have three inversion-points for each inversion-temperature lying within certain limits, less than the critical temperature; otherwise, for a given isopiestic, there is only one inversion-point for each inversion-temperature. It may, however, not be possible to obtain these experimentally, for other reasons.

for air is the isopiestic for one atmosphere, when the expansions deal with pressures such as those given by Olszewski. The same thing is brought out even more clearly by a little consideration of the apex of the curvilinear figure BDEB' in fig. 2, say, the portion lying between the ordinates y=5.7 and y=6.75. The parabola DE gives the maximum initial pressures possible for expansion into a vacuum as the temperatures fall from 6.75. The coresponding curve of maximum pressures for expansion against the pressure of one atmosphere will be very slightly below DE. This shows clearly the fall of initial pressure with a rising inversion-temperature. Olszewski's air results are approximately represented by the hyperbola

 $\alpha(4.16-y)=0.61, \dots (38)$ 

whereas the theoretical line is very near DE, whose equation is

$$y^2 = -\frac{27}{16}(\alpha - 27).$$
 (34)

The conclusion seems to be that the Olszewski experiment, although an expansion experiment like the Joule-Kelvin experiment, differs essentially from it. We may ask where the differences appear. They seem to embrace at least the following:-We may amplify the analytical condition of the Joule-Kelvin experiment and consider it to involve the constancy of the function U + K + pv, where K is the kinetic energy of the gas. In the Joule-Kelvin experiment, K is so small, both before and after the gas passes the porous plug, that it may be neglected. The same result might be attained if the values of K before and after passing the plug were approximately equal. In the Olszewski experiment it is clear that the value of K before the gas reaches the nozzle is small; but it is by no means small after passing the nozzle. From the numerical data so far published for the hydrogen experiment, the value of K after passing the plug must be comparable with the value of pv at the critical point, on the basis of van der Waals's equation \*. Again, Olszewski in the hydrogen paper already referred to, states † that "the expansion took place slowly and lasted from 4 to 5 seconds." But in the experiments of Joule and Kelvin associated with their main porous-plug experiments, they found that on either opening or shutting a certain stop-cock, after the temperature of the air had become pretty constant, fluctuations of temperature continued to be very perceptible in different cases for periods of from 3 or 4 minutes up to

<sup>\*</sup> See Note at end. † Loc. cit. p. 539. ‡ Kelvin, Coll. Works, vol. i. p. 359; and generally pp. 357-362.

nearly half an hour after the pressure had become sensibly uniform. They add that having discovered this fact, they found it necessary to delay recording the observations until  $1\frac{1}{2}$  or 2 hours after the pumps began working. Further, Joule and Kelvin commenced by using an aperture in the nozzle, but gave this up in favour of a porous plug. Their purpose\* was "in order that the work done by the expanding fluid may be immediately spent in friction without any appreciable portion of it being even temporarily employed to generate  $vis\ viva$ , or being devoted to produce sound." Olszewski apparently continues to use the small aperture †. These appear to be essential differences in the conduct of the two experiments. In any case Professor Olszewski's further detailed description of the experimental arrangements and of the apparatus will be awaited with interest.

It is worthy of note that if Joule-Kelvin experiments were to be carried out for points on the envelope MLN, the kinetic energy would in every case be so small that it might be neglected. Such experiments, by the actual determination of the envelope, would further our insight into the nature of gases as subject, or not, to van der Waals's law. It would also be possible to conduct them with comparative ease, for the ranges of pressure and temperature are neither too great, nor do they extend into regions too difficult of access. For air, B is about 100° abs. and D is about 850° abs., while the highest pressure need not exceed some 350 atmospheres. For hydrogen, B is a little above its boiling-point, D is not far from the melting-point of carbonic acid, and the highest pressure necessary would not exceed 135 atmospheres.

In 1902, on the appearance of Professor Olszewski's paper on the inversion-temperature of hydrogen, I calculated inversion-temperatures (although they were not published) on the basis of van der Waals's, Clausius's, and Reinganum's equations. The results gave the connexion between this temperature and the associated volumes of the gas at high and at low pressure. The van der Waals's formula has been the subject of the present paper, and is given in equation (8) or (9). From Clausius's equation

$$p = \frac{Rt}{v - \alpha} - \frac{c}{t(v + \beta)^2}, \qquad (39)$$

we get

$$t^2 = t_c^2 \frac{27}{8} \frac{\alpha + \beta}{\alpha} \frac{(v - \alpha)(v - \alpha')\{3vv' + 2\beta(v + v') + \beta^2\}}{(v + \beta)^2(v' + \beta)^2}, \quad (40)$$

<sup>\*</sup> Kelvin, Coll. Works, vol. i. p. 346. † See note at end.

which, when the pressures differ only by a small amount, becomes

$$t^{2} = t_{c}^{2} \frac{27}{8} \frac{\alpha + \beta}{\alpha} \frac{(v - \alpha)^{2} (3v + \beta)}{(v + \beta)^{3}}, \quad (41)$$

and, when the pressures are themselves small, reduces to

$$t = t_c \frac{9\sqrt{2}}{4} \sqrt{1 + \frac{\beta}{\alpha}}. \qquad (42)$$

From Reinganum's equation

$$p = \frac{Rtv^3}{(v-b)^4} - \frac{a}{v^2}, \quad . \quad . \quad . \quad (43)$$

where a and b are constants, we get in like manner the equations

$$\mathbf{R}t = \frac{2a}{b} \frac{(v-b)(v'-b)}{vv'} \frac{(v-b)^3(v'-b)^3}{\{2vv'-b(v+v')\}\{2v^2v'^2-2bvv'(v+v')+b^2(v^2+v'^2)\}},$$

giving, for nearly equal pressures,

$$Rt = \frac{a}{2b} \left( \frac{v - b}{v} \right)^5, \quad . \quad . \quad . \quad (45)$$

and when the pressures also are small

$$Rt = \frac{a}{2b}. \qquad . \qquad . \qquad . \qquad . \qquad (46)$$

The critical temperature, on Reinganum's equation, is

$$Rt_{c} = \left(\frac{2 + 2\sqrt{6}}{3 + 2\sqrt{6}}\right)^{5} \frac{1}{3 + \sqrt{6}} \frac{a}{b} \stackrel{\cdot}{=} \cdot 0933 \frac{a}{b} . \quad . \quad (47)$$

Berthelot\* in two great memoirs has discussed the theory of the equation of state, especially for low pressures, in a thoroughly exhaustive manner. His comparison of theory with experiment has led him to formulate a modified form of van der Waals's equation for moderate pressures, namely,

$$p = \frac{Rt}{v - b} - \frac{a}{tv^2}, \qquad (48)$$

but with the understanding that instead of the critical constants being derived from a, b, and R, the constants to be chosen are  $t_c$ ,  $p_c$ , and R, with the relations

$$b = \frac{1}{4}v_c$$
,  $a = \frac{27}{64} \frac{R^2 t_c^3}{p_c}$ , and  $v_c = \frac{9}{32} \frac{R t_c}{p_c}$ . (49)

\* 'Livre Jubilaire dedié à H. A. Lorentz,' 1900, p. 417. "Sur les thermomètres à Gaz," Trav. et Mém. du Bur. Intern. des Poids et Mesures, 1903.

These four equations of state give for the maximum value of the temperature of inversion

$$6.75t_c$$
,  $3.182\sqrt{1+\frac{\beta}{\alpha}}t_c$ ,  $5.36t_c$ , and  $4.24t_c$ ,

respectively. For carbonic acid  $\alpha$  and  $\beta$  are nearly equal in Clausius's equation, so that for this gas the limiting temperature of inversion is  $4.5\,t_c$ .

In conclusion, the subject of the above discussion has been the possibility of coincidence between Professor Olszewski's experiment and that of Dr. Joule and Lord Kelvin with the porous-plug, guided by van der Waals's equation of state. That this equation requires some modification, or at least entails a limitation in its applicability to all gases and in all conditions, is admitted; and it may even be that the Olszewski experiment and the van der Waals's equation may each assist the other in the progress towards truth; but, today, on the conditions assumed, there is apparent incompatibility between them. This does not at all affect the purpose, as I read it, of Professor Olszewski's experiment, nor its success, namely, the determination of a temperature suitable for moderate pressures, such that if expansion of a gas be made below that temperature, cooling will take place. Incidentally, the full meaning of the term "a Joule-Kelvin inversion-temperature" has been developed; and whatever form the fundamental equation of state may ultimately take, this meaning will probably not require alteration. Although the theory is simple, the calculations involved have been long and heavy, but it is hoped that, as nearly every one was repeated, no serious errors have crept in.

Note.—The texts at one point in the description of Professor Olszewski's experiment are confusing. The German text of the Krakau Bulletin (1901, p. 455) speaks of "die im Innern mit Sämischleder ausgefütterte Blechbuchse." The translation from this in 'Nature' (lxv. p. 577, April 1902) is "a thin metal box which is lined with chamois leather." The translation in the Phil. Mag. iii. p. 537, May 1902) is "box . . . which is stuffed with chamois leather." The difference between stuffing and lining the box materially alters the question. A German friend, who is a well-known authority on the German language, tells me that ausgefütterte means "lined, as a glove lines the hand." The detailed description of the experiment promised by Professor Olszewski will, however, clear up the matter.

Peterhouse, Cambridge, October 1907. X. On the Thermally excited Vibrations of an Atmosphere. By C. V. Burton, D.Sc.

IN Lord Rayleigh's paper "On the Vibrations of an Atmosphere," † the free vibrations of a gaseous mass in certain sphere," † the free vibrations of a gaseous mass in certain ideal circumstances are investigated. In the present note an attempt is made to carry the investigation a step further by considering the vibrations which in like circumstances arise from fluctuating thermal conditions; the problem presented in each case being the determination of the pressure as a function of time and coordinates when the thermal conditions are specified.

Equations of a gas subject to small fluctuations of thermal state, but otherwise at rest.

It will be convenient to prefix the symbol  $\delta$  to indicate the disturbances of the various quantities involved, as arising from the given small thermal fluctuations.

 $\rho$  is the density at any point when there is no disturbance;  $\rho + \delta \rho$  the density when disturbances are present;

T,  $T + \delta T$  the undisturbed and disturbed (absolute) temperature at any point;

 $p, p + \delta p$  pressure;

u, v, w are the velocity-components at any point in the disturbed condition, and vanish when disturbances are

R as usual stands for  $p/\rho T$ , and is an absolute constant.

Thus  $RT = p/\rho = (\text{velocity of sound})^2$  when Boyle's law is applicable  $=a^2$  suppose . . . . . . (1)

The equation of continuity is

$$\frac{\partial(\rho+\delta\rho)}{\partial t} + \frac{\partial\{(\rho+\delta\rho)u\}}{\partial x} + \frac{\partial\{(\rho+\delta\rho)v\}}{\partial y} + \frac{\partial\{(\rho+\delta\rho)w\}}{\partial z} = 0, \quad (2)$$

where  $\partial/\partial t$  is time-differentiation at a point fixed in space. That is, to a first order,

$$\frac{\partial \delta \rho}{\partial \delta t} + \frac{\partial (\rho u)}{\partial (\rho u)} + \frac{\partial \gamma}{\partial (\rho v)} + \frac{\partial z}{\partial (\rho w)} = 0. \quad . \quad . \quad (3)$$

\* Communicated by the Author.

<sup>† &#</sup>x27;Collected Papers,' vol. iii. p. 335; Phil. Mag. vol. xxix. 1890, pp. 173-180. L 2

Again,

$$\frac{\partial^{\delta p}}{\partial t} = R\rho \frac{\partial^{\delta T}}{\partial t} + RT \frac{\partial^{\delta \rho}}{\partial t} 
= R\rho \frac{\partial^{\delta T}}{\partial t} - RT \left[ \frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} + \frac{\partial(\rho w)}{\partial z} \right].$$
(4)

To a first order also, when V is the gravitation potential \*,

$$\rho\left(\frac{\partial u}{\partial t}, \frac{\partial v}{\partial t}, \frac{\partial w}{\partial t}\right) = -\left[(\rho + \delta\rho)\frac{\partial V}{\partial x} + \frac{\partial(\rho + \delta\rho)}{\partial x}, \dots, \dots\right], \quad (5)$$

that is (since  $\rho$  is not a function of t)

$$\frac{\partial(\rho u)}{\partial t}, \frac{\partial(\rho v)}{\partial t}, \frac{\partial(\rho w)}{\partial t} = -\left[\delta\rho \frac{\partial V}{\partial x} + \frac{\partial \delta\rho}{\partial x}, \dots, \dots\right]. \quad (5')$$

From (4), (5'), and (1) we obtain

$$\frac{\partial^{2}\delta p}{\partial t^{2}} = \operatorname{R}\rho \frac{\partial^{2}\delta T}{\partial t^{2}} + \operatorname{RT} \left[ \frac{\partial \delta \rho}{\partial x} \cdot \frac{\partial V}{\partial x} + \frac{\partial \delta \rho}{\partial y} \cdot \frac{\partial V}{\partial y} + \frac{\partial \delta \rho}{\partial z} \cdot \frac{\partial V}{\partial z} + \delta \rho \nabla^{2}V + \nabla^{2}\delta p \right] 
= \operatorname{R}\rho \frac{\partial^{2}\delta T}{\partial t^{2}} + a^{2}\nabla^{2}\delta p + a^{2} \left( \frac{\partial \delta \rho}{\partial x} \cdot \frac{\partial V}{\partial x} + \frac{\partial \delta \rho}{\partial y} \cdot \frac{\partial V}{\partial y} + \frac{\partial \delta \rho}{\partial z} \cdot \frac{\partial V}{\partial z} \right), \quad (6)$$

provided that  $\nabla^2 V = 0$ .

When there are no impressed forces capable of influencing the motion, the last principal term on the right hand of (6) disappears. When in addition there are no changes of temperature, the first term on the right hand also vanishes and (6) reduces to the well-known form appropriate to small disturbances in a gas obeying Boyle's law.

When no forces act on the gas we have from (5), to a first

order,

$$\left(\frac{\partial u}{\partial t}, \frac{\partial v}{\partial t}, \frac{\partial w}{\partial t}\right) = -\frac{1}{\rho} \left(\frac{\partial \delta p}{\partial x}, \frac{\partial \delta p}{\partial y}, \frac{\partial \delta p}{\partial z}\right);$$

so that, if  $\Delta u$ , . . . are increments corresponding to a finite lapse of time,

$$(\Delta u, \Delta v, \Delta w) = -\frac{1}{\rho} \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \int \delta p \, dt \; ; \quad . \quad (7)$$

 $\rho$  being by definition independent of t. If we are dealing with gas which is uniform in the undisturbed state,  $\rho$  is everywhere and always constant, and (7) shows that, in this case to our order of approximation, if u, v, w at any time satisfy

<sup>\*</sup> Defined, for any given point, as the work to be done against gravitative forces in bringing unit mass from infinity up to that point.

the irrotational condition (for example, if 0=u=v=w initially) they will continue to do so throughout the motion.

Equation (6) may also be put into another form, which we shall find convenient. For if  $\gamma$  is the ratio of the two specific heats of the gas, it can be shown that

$$R\rho \frac{\partial \delta T}{\partial t} = \frac{\gamma - 1}{\gamma} \left( \frac{\partial \delta p}{\partial t} + \rho \frac{\partial H}{\partial t} \right), \quad . \quad . \quad (8)$$

where  $\partial H/\partial t$  is the value at any point of the rate at which heat is being received per unit mass.

Using (8), we have in place of (6)

$$\frac{\partial^{2} \delta p}{\partial t^{2}} = (\gamma - 1) \rho \frac{\partial^{2} H}{\partial t^{2}} + \gamma u^{2} \nabla^{2} \delta p + \gamma u^{2} \left( \frac{\partial \delta \rho}{\partial x} \cdot \frac{\partial V}{\partial x} + \frac{\partial \delta \rho}{\partial y} \cdot \frac{\partial V}{\partial y} + \frac{\partial \delta \rho}{\partial z} \cdot \frac{\partial V}{\partial z} \right). (9)$$

Consider next an atmosphere such as Lord Rayleigh has discussed in his paper already referred to. This atmosphere is bounded below by a plane, which we take as the plane of xy, while in all other directions it is unlimited. The acceleration g due to gravity acts everywhere perpendicularly to this plane (that is parallel to the axis of z) and is of uniform intensity.

In the undisturbed state the density  $\rho$  is given by

$$\rho = \rho_0 e^{-\frac{g}{a^2}z}$$
, while  $p = p_0 e^{-\frac{g}{a^2}z}$ ; . . . (10)

the "undisturbed" temperature T being everywhere uniform.

Let the given thermal conditions which cause the disturbance be expressed by

so that at each instant every plane parallel to yz is an isothermal surface; the additional temperature-distribution  $\delta T$  being made to travel through the atmosphere in the direction of increasing x, like a progressive wave-train. The disturbance of pressure due to  $\delta T$  will evidently be of the form

$$\delta p = \varpi e^{i(kx-nt)}, \ldots \ldots (12)$$

 $\infty$  being a function of z.

From (6), remembering that

$$\frac{\partial \mathbf{V}}{\partial z} = +g$$
, while  $a^2 \frac{\partial \delta \rho}{\partial z} = \frac{\delta \rho}{\partial z}$ 

(because T and  $\delta$ T are independent of z), we obtain

$$\nabla^2 \delta p + \frac{g}{a^2} \cdot \frac{\partial \delta p}{\partial z} - \frac{1}{a^2} \frac{\partial^2 \delta p}{\partial t^2} = -\frac{R\rho}{a^2} \frac{\partial^2 \delta T}{\partial t^2}. \quad (13)$$

Substituting in this from (11) and (12), and using (10),

$$\frac{\partial^2 \varpi}{\partial z^2} + \frac{g}{a^2} \frac{\partial \varpi}{\partial z} + \left(\frac{n^2}{a^2} - k^2\right) \varpi = \frac{R\beta}{a^2} \rho_0 e^{-\frac{gz}{a^2}}; \quad . \quad (14)$$

a solution of which is

$$\varpi = \frac{R\beta \rho_0 n^2}{n^2 - k^2 a^2} \cdot e^{-\frac{gz}{a^2}},$$

$$\delta p = \frac{R\beta \rho_0 n^2}{n^2 - k^2 a^2} \cdot e^{-\frac{gz}{a^2} + i(kx - nt)}.$$
(15)

or

This solution corresponds to the forced vibrations, arising from the temperature-changes expressed by  $\delta T$ . The most general solution of (14) is found by adding to (15) the solution of (14) with its right-hand member replaced by zero. Such an addition would represent free vibrations, and it may be remarked in passing that the equation formed by equating to zero the left-hand member of (14) is equivalent to (27) of Lord Rayleigh's paper. It should, however, be remembered that the quantity there denoted by  $\rho$  would in our notation be  $\delta \rho/\rho$ .

By means of (5), bearing in mind the periodic character

of the motion, it is easily verified that

$$u = -\frac{R\beta kn}{n^2 - k^2a^2}e^{i(kx - nt)}, v = 0, w = 0.$$
 (16)

Since w vanishes throughout, it follows that the motion would not be modified (fluid friction apart) if any number of constraints were introduced in the form of fixed rigid horizontal planes. For these thermally excited vibrations, then, the solution has the same form whether we suppose the atmosphere unlimited upward, or whether we consider a thin lamina of air between two neighbouring horizontal planes.

As Lord Rayleigh has done in the case of free vibrations \*, and with much the same degree of plausibility, we may pass from the consideration of a thin flat lamina of air to that of a thin spherical sheet. In view of what has just been said concerning the simpler problem, it seems that the thermally-excited vibrations of such a sheet of air should not differ widely from those of an outwardly unlimited atmosphere. The object here is to obtain some analogy to the barometric variations which arise from diurnal heating and cooling. The problem considered is not that of the earth's atmosphere, but it may be hoped that it is not too remote from actual conditions to afford some light thereon.

Following Lord Rayleigh, all amplitudes concerned are treated as small, the mean temperature is taken as uniform over the whole of the spherical sheet considered, and of course the limitations imposed by the thinness of the sheet preclude any systematic motion of the air corresponding to trade-winds or the like.

It will be assumed that in the free vibrations of the spherical sheet, the relation between density and pressure follows the adiabatic law; so that in the case of thermally excited vibrations the only transfer of heat of any account is that arising from the heating-effect of the sun and from radiation into space, no appreciable effect being produced by the passage of heat horizontally from one part of the atmosphere to another. Accordingly (9) is the form of equation appropriate to the problem, gravity, however, being evidently without perceptible effect on the motion, so that the last principal term onthe right hand may be omitted. Thus

$$\frac{\partial^2 \delta p}{\partial t^2} = (\gamma - 1) \rho \frac{\partial^2 \mathbf{H}}{\partial t^2} + \gamma a^2 \nabla^2 \delta p. \quad . \quad . \quad (17)$$

To represent roughly the heating-effect of the sun, it is assumed that, during the day, heat is being gained per unit mass of air at a rate proportional to the sine of the sun's altitude; while, day and night, heat is being lost per unit mass at a rate proportional to the fourth power of the absolute temperature of the air. As the fluctuations above and below the mean temperature in any latitude are supposed to besmall, the rate of loss referred to may be treated as constant.

Taking, for simplicity, the time of an equinox, let  $\theta = co$ 

latitude,  $\omega =$ longitude.

Then  $\sin (\operatorname{altitude of sun}) = \sin (kt - \omega) \sin \theta$ ,  $\frac{2\pi}{k}$  being a solar day, and the origin of time being sunrise at the meridian

Our assumptions are thus expressed by

$$\frac{\partial \mathbf{H}}{\partial t} = \mathbf{A} \sin (kt - \boldsymbol{\omega}) \sin \theta - \mathbf{B} \mathbf{T}^{4}, \\
\text{when } 0 < kt - \boldsymbol{\omega} < \boldsymbol{\pi}; \\
\frac{\partial \mathbf{H}}{\partial t} = -\mathbf{B} \mathbf{T}^{4}, \\
\text{when } \pi < kt - \boldsymbol{\omega} < 2\pi.$$
(18)

To our order of approximation, dH=0 for any whole day. which leads to

$$BT^4 = \frac{A \sin \theta}{\pi} \dots \dots (19)$$

This corresponds to absolute zero of temperature at the poles; we are more concerned, however, with the diurnal changes, which probably furnish a better representation of actual conditions than do the mean temperatures for different latitudes deduced from our assumptions. From (18) and (19),

$$\frac{\partial H}{\partial t} = A \sin \theta \left\{ \sin (kt - \omega) - \frac{1}{\pi} \right\}, \text{ when } 0 < kt - \omega < \pi;$$

$$\frac{\partial H}{\partial t} = -\frac{A \sin \theta}{\pi}, \text{ when } \pi < kt - \omega < 2\pi. \qquad (20)$$

Also

$$\frac{\partial^{2} \mathbf{H}}{\partial t^{2}} = \mathbf{A}k \sin \theta \cos (kt - \boldsymbol{\omega}), \text{ when } 0 < kt - \boldsymbol{\omega} < \boldsymbol{\pi};$$

$$\frac{\partial^{2} \mathbf{H}}{\partial t^{2}} = 0, \text{ when } \boldsymbol{\pi} < kt - \boldsymbol{\omega} < 2\boldsymbol{\pi}. \qquad (21)$$

It is now proposed to examine the disturbances of pressure arising from the temperature-disturbances (21) imagined as affecting a spherical sheet of air whose mean temperature is uniform.

Expanding  $\partial^2 H/\partial t^2$  in a Fourier series we find

$$\frac{\partial^{2} \mathbf{H}}{\partial t^{2}} = \frac{1}{2} \mathbf{A} k \sin \theta \cos (kt - \omega) - \frac{4}{3\pi} \mathbf{A} k \sin \theta \sin 2 (kt - \omega) + \text{terms of higher frequency.}$$
(22)

The right hand of this equation must now be expanded in such a form that  $\theta$ ,  $\omega$  appear only in a series of surface harmonics. It can be shown that (22) is equivalent to

$$\frac{\partial^{2} \mathbf{H}}{\partial t^{2}} = \frac{1}{2} \mathbf{A} k \sin \theta \cos (kt - \omega) - \mathbf{A} k \left\{ \frac{15}{32} \sin^{2} \theta \sin 2 (kt - \omega) + \frac{5}{64} \sin^{2} \theta (7 \cos^{2} \theta - 1) \sin 2 (kt - \omega) \right\}$$

+ 
$$\frac{6435}{354304}$$
 sin<sup>2</sup>  $\theta$  (33 cos<sup>4</sup>  $\theta$  – 18 cos<sup>2</sup>  $\theta$  + 1) sin 2 ( $kt - \omega$ ) + ...}  
+ terms of higher frequency; . . . . . . . (23)

in which the first term, considered as a function of  $\theta$ ,  $\omega$  is a surface harmonic of degree 1, and the terms given within the bracket of degrees 2, 4, 6 respectively. For convenience let

us write

R.H. member of 
$$(23) \equiv S_1 \cos kt + S_1' \sin kt + (S_2 + S_4 + S_6 + ...) \cos 2kt + (S_2' + S_1' + S_6' ...) \sin 2kt + ...$$
 (24)

where each S is a surface harmonic (of degree indicated by the suffix) multiplied by a constant physical factor. For the determination of the disturbance of pressure  $\delta p$ , we may assume provisionally a solution of (17) in the form

$$\delta p = Q_1 \cos kt + Q_1' \sin kt + (Q_2 + Q_4 + Q_6 + \dots) \cos 2kt + (Q_2' + Q_4' + Q_6' + \dots) \sin 2kt + \dots; \quad (25)$$

the Q's being also surface harmonics multiplied by constant physical factors. Now

$$\nabla^2 \delta p = \frac{\partial^2 \delta p}{\partial r^2} + \frac{2}{r} \frac{\partial \delta p}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \delta p}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \delta p}{\partial \omega^2}, (26)$$

and if q is the outward radial velocity of the air at any point within the spherical sheet, we have from (5), taking the axis (say) of z vertically upward,

$$\rho \frac{\partial q}{\partial t} = -\frac{\partial \delta p}{\partial r} (\rho \text{ being independent of } t). \quad (27)$$

But q vanishes at both spherical boundaries of the sheet, the radii of which may be called r and  $r+\Delta r$ : hence when  $\Delta r$  is very small, q is evidently insignificant throughout the motion; so that

$$\frac{\partial q}{\partial t} = 0$$
, and  $\frac{\partial \delta p}{\partial r} = 0$ . . . . (28)

Also 0 = (q at outer boundary) - (q at inner boundary)=  $\partial q/\partial r\Delta r$ , so that  $\partial q/\partial r = 0$  always.

Hence by (27) 
$$\partial^2 \delta p / \partial r^2 = 0, \dots (29)$$

which justifies our assumption that  $\delta p$  is independent of r. Using (28) and (29), (26) becomes

$$\nabla^{2}\delta p = \frac{1}{r^{2}} \left\{ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^{2}\theta} \frac{\partial^{2}}{\partial\omega^{2}} \right\} \left\{ Q_{1}\cos kt + Q_{1}'\sin kt + (Q_{2} + Q_{4} + Q_{6} + \dots)\cos 2kt + (Q_{2}' + Q_{4}' + Q_{6}' + \dots)\sin 2kt \right\}$$

$$= -\frac{1 \cdot 2}{r^{2}} \left( Q_{1}\cos kt + Q_{1}'\sin kt \right) - \frac{2 \cdot 3}{r^{2}} \left( Q_{2}\cos 2kt + Q_{2}'\sin 2kt \right)$$

$$-\frac{4 \cdot 5}{r^{2}} \left( Q_{4}\cos 2kt + Q_{4}'\sin 2kt \right) - \frac{6 \cdot 7}{r^{2}} \left( Q_{6}\cos 2kt + Q_{6}'\sin 2kt \right)$$

$$= -\frac{3}{r^{2}} \left( Q_{4}\cos 2kt + Q_{4}'\sin 2kt \right) - \frac{6 \cdot 7}{r^{2}} \left( Q_{6}\cos 2kt + Q_{6}'\sin 2kt \right)$$

$$= -\frac{3}{r^{2}} \left( Q_{4}\cos 2kt + Q_{4}'\sin 2kt \right) - \frac{6 \cdot 7}{r^{2}} \left( Q_{6}\cos 2kt + Q_{6}'\sin 2kt \right)$$

$$= -\frac{3}{r^{2}} \left( Q_{4}\cos 2kt + Q_{4}'\sin 2kt \right) - \frac{6 \cdot 7}{r^{2}} \left( Q_{6}\cos 2kt + Q_{6}'\sin 2kt \right)$$

by a well known property of surface harmonics.

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By means of (24), (25), and (30), (17) may be written

$$\left(k^{2}-1 \cdot 2 \frac{\gamma a^{2}}{r^{2}}\right) (Q_{1} \cos kt + Q_{1}' \sin kt)$$

$$+ \left(4k^{2}-2 \cdot 3 \frac{\gamma a^{2}}{r^{2}}\right) (Q_{2} \cos 2kt + Q_{2}' \sin 2kt)$$

$$+ \left(4k^{2}-4 \cdot 5 \frac{\gamma a^{2}}{r^{2}}\right) (Q_{4} \cos 2kt + Q_{4}' \sin 2kt)$$

$$+ \left(4k^{2}-6 \cdot 7 \frac{\gamma a^{2}}{r^{2}}\right) (Q_{6} \cos 2kt + Q_{6}' \sin 2kt)$$

$$+ \dots$$

$$= S_{1} \cos kt + S_{1}' \sin kt + (S_{2}+S_{4}+S_{6}+\dots) \cos 2kt$$

$$+ (S_{2}'+S_{4}'+S_{6}'+\dots) \sin 2kt + \dots$$

$$(31)$$

By equating terms in  $\cos kt$ ,  $\sin kt$ , ... we obtain

$$(Q_1 \cos kt + Q_1' \sin kt) \left(k^2 - 1 \cdot 2 \frac{\gamma a^2}{r^2}\right) = -(\gamma - 1)\rho(S_1 \cos kt + S_1' \sin kt)$$

$$= -\frac{1}{2}(\gamma - 1)A\rho k \sin \theta \cos (kt - \omega)$$

by (24); with corresponding values for  $Q_2 \cos 2kt + Q_2' \sin 2kt$ , &c.

Substituting in (25) the values thus obtained, we have finally for the solution corresponding to (thermally) forced vibrations,

It is unfortunately very difficult to base any sort of numerical estimate on these tentative results. In agreement with Lord Rayleigh's investigation the denominator of the first term of  $\delta p$  vanishes when  $k = \sqrt{\gamma a^2} \sqrt{2}/r$ ;  $\gamma a^2$  being here the quantity which Lord Rayleigh denotes by  $a^2$ . Similarly the denominator of the second term vanishes when  $2k = \sqrt{\gamma a^2} \sqrt{6}/r$ . It appears that both the denominators are small, corresponding to well-marked resonance-effects; but we cannot even say with certainty what is the sign of each.

We are dealing in fact with just that degree of isochronism between the free periods of the spherical sheet of air and the periods of the (thermal) disturbing agency for which our assumption of no dissipation ceases to represent even approxi-

mately the actual conditions.

It may be remarked, however, that the value of  $\delta p$  given by (32) indicates a semi-diurnal barometric amplitude not widely different from the diurnal, provided equally favourable resonance conditions may be assumed. If the agreement of period between free vibrations and disturbing agency were somewhat better for the second term of  $\delta p$  than for the first, the greater prominence of the semi-diurnal period might perhaps be accounted for.

A less remote representation of atmospheric conditions might have been realized by introducing into the value of  $\partial H/\partial t$  an additional factor, a function of co-latitude and longitude, so as to take some account of the fact that the diurnal variation of temperature is greater over a continent than over an ocean. Such a factor, however, is not competent to introduce into the barometric fluctuations at a given station terms whose periods are submultiples of that of the thermal

XI. On the Use of Variable Mutual Inductances. ALBERT CAMPBELL, B.A.\* (From the National Physical Laboratory.)

Plate IX.

CONTENTS.

1. Introductory.

excitation.

2. Mutual versus Self Inductance.

3 & 4. Construction and Adjustment of Variable Mutual Inductances.
 6, 7 & 8. Uses of the same for measuring unknown Mutual Inductance, Self Inductance, and Capacity.
 Appendix. The Scale of the Excentric-Coil Mutual Inductance.

## 1. Introductory.

THE accurate measurement of small self-inductances and capacities has of late years assumed an increased importance owing to its direct practical application in connexion with wireless telegraphy; and much important and interesting work has been done on the subject especially as: regards the calculation and measurement of self inductance. For some time past I have found that suitably designed mutual inductances are of the greatest assistance in such measurements, and I incline to think that by their use some

\* Communicated by the Physical Society: read October 25, 1907.

of the sources of error inherent in other methods are avoided. The chief method (B) here described was designed for the measurement of the small self inductances (1 to 200 microhenries) used in wave telegraphy, and it has proved most useful in such work. Before I proceed to describe the designs and the methods of use which I have found valuable, let us consider and compare mutual and self inductances in relation to their capabilities in practical use.

## 2. Mutual versus Self Inductance.

For a number of reasons mutual inductances are more easily dealt with than self inductances. Those of invariable value, when properly designed, have the following advantages:-

(a) The absolute values can be calculated with much more certainty from the geometrical dimensions, since the formulas for mutual inductance are of high theoretical accuracy while those for self inductance are much less satisfactory \*.

(b) Unless the conductors are highly stranded, the current distribution varies with frequency and in general the self inductance will also vary. By keeping the two circuits at a relatively large distance from one another the mutual induc-

tance is practically free from this effect.

(c) The effects of distributed capacity are probably less in mutual than in self inductances. In all cases the distributed capacity of one of the two coils can be made very small by sufficiently decreasing the number of turns in it (or opening them apart) while increasing the number in the other coil to keep the M constant.

When the mutual inductance is of the variable type, it can always be designed so that its value can be varied continuously from negative to positive through zero. This is a very great advantage, for with variable self inductance standards the incapability of reaching a zero value is a distinct drawback.

## 3. Construction of Variable Mutual Inductances.

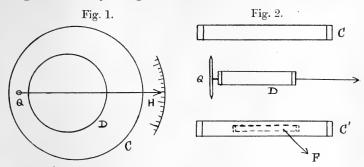
For short range standards the construction used by Lord Rayleigh may be employed †. In this the primary coil is inside the secondary and can be rotated round a common diameter as in the Ayrton-Perry variable self inductances, and the whole positive range is comprised within 90° of turning, which gives a scale not nearly open enough for

† Phil. Mag. vol. xxii. pp. 469-500 (1886); Collected Papers, vol. ii. p. 155.

<sup>\*</sup> For example see Rosa, Bull. Bur. Stands. vol. ii. p. 161 (1906); and Strasser, Ann. der Phys. vol. xviii. p. 763 (1905).

high accuracy. I have therefore designed a different and more elaborate arrangement which gives a much more extended scale. I proceed to describe the first model, which has been in use for a considerable time with most satisfactory results.

The general arrangement of the apparatus is shown diagrammatically in figs. 1 and 2, which are plan and side



The primary \* circuit consists of two view respectively. equal coaxial coils C and C', which are connected in series, their windings being in the same direction of turning. The secondary consists of the coils D and F in series. Of these coils, D is movable, being mounted on an excentric axis Q so as to be free to turn in a plane parallel to those of C and C' and midway between them. Rigidly connected with the movable coil is a pointer H which moves over a circular scale of about 180° in extent and graduated to read directly. The coil F is subdivided into ten sections, which are in series, each of them being 0.1 millihenry, and their junctions are brought to a set of separate terminals or studs with a turning head. The range of the moving coil extends from -0.002 to +0.11 millihenry. This gives a continuous range from 0 up to 1 millihenry, readable near zero to 0.02 microhenry, to 1 part in 500 at 0.1 millihenry, and to 1 in 5000 at 1 millihenry. The subdivision of the coil F is easily carried out by the following artifice. The coil is wound with uniformly stranded wire of ten insulated strands, all the strands are connected in series, and the whole adjusted to give 1 millihenry †. If the stranding has been properly

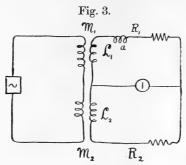
† Mutual Inductances with stranded wires were used many years ago by Prof. Brillouin (*Thèses presentées à la Faculté des Sciences de Paris*, 1882).

<sup>\*</sup> It is only for convenience of description that the circuits are here distinguished as *primary* and *secondary*. They are really quite interchangeable.

done, it will be found that no one of the sections differs from its neighbours by more than 1 part in 1000, and each is 0.1 millihenry. The placing of the movable secondary coil midway between the planes of the two primary ones ensures that small axial displacements shall have very little effect on the mutual inductance.

#### 4. Adjustment and Calibration of Variable Mutual Inductances.

The equality of any pair of sections can be tested by connecting them in series with their windings in opposition in circuit with a ballistic galvanometer and reversing the current in the primary. It should be noticed here that, if a primary coil have any number of secondary circuits, the mutual inductance to all the secondaries in series is equal to the algebraic sum of their separate mutual inductances (+ or according to the direction of the winding). Owing to this very important property we can build up and step down in the values as easily as if we were dealing with resistances, and there is the further simplification that we can subtract as well as add the values. The marking of the scale and the setting of the coil F are done by comparison with a fixed standard mutual inductance such as I have described elsewhere\*. The comparison may be made by Maxwell's method †, using a sensitive ballistic galvanometer or a vibration galvanometer as detector. When a vibration galvanometer is used as in fig. 3, it should be remembered that, for a



balance, two conditions must be satisfied, viz.,

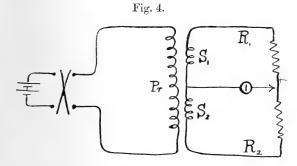
$$\begin{aligned} &M_1/M_2 \!=\! R_1/R_2\\ &\text{and} &L_1/L_2 &=\! R_1/R_2, \end{aligned}$$

<sup>\*</sup> Phys. Soc. May 1907; Phil. Mag. [6] vol. xiv. p. 494, Oct. 1907. Also see Proc. Roy. Soc. A. vol. lxxix. p. 428, June 5, 1907.
† Maxwell, Elect. and Mag. 2nd edition, ii. § 755.

where  $R_1$  and  $R_2$  include the resistances of the secondary coils. In order that the second condition may hold, it is necessary to introduce into one of the secondary branches a coil a whose self inductance can be continuously varied; by alternate adjustments of  $R_1/R_2$  and the self inductance of this coil, a balance is easily obtained. The fact that  $R_1$  and  $R_2$  are partly of copper coils is apt to introduce some inaccuracy. The copper resistance, however, can usually be largely swamped without losing too much of the sensitivity.

In connexion with this method I may mention that it is perfectly applicable to the case of comparing the mutual inductances between one primary circuit and two separate

secondaries. This case is shown in fig. 4.



By this means a thorough intercomparison (or adjustment) can be made between the various sections of a subdivided mutual inductance. By further sets of secondary coils for higher multiples (10, 100, and so on) any desired range may be obtained. By stranding (or otherwise subdividing) the primary coils as well as the secondary ones a multiple-range inductance is the result. In all cases the subdivision can be effected by other means than stranding the wires, which is merely used to avoid the separate adjustment of the sections. The main objection to the subdivision by stranding is that it increases the distributed capacity of the coils. With coils of many turns this might be a serious drawback, but with the relatively few turns required for 1 millihenry the effect can only be very small and I have not yet noticed it in It should be kept in mind that, as in all standard inductances, eddy currents should be prevented by using only highly stranded wire for the winding of every section and by avoiding the use of any metal parts near the coils.

By varying the relative dimensions and positions of the two fixed primary coils CC' (fig. 2) and the movable

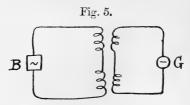
secondary D, the scale can be considerably modified, and can be designed to suit special purposes. The most generally useful type of scale becomes more and more open as the readings approach zero, for this gives good accuracy of reading even at very low values. Fortunately in the present instance this type of scale can readily be attained. Further discussion of this point will be found in an Appendix.

## 5. Employment of Variable Mutual Inductances.

Variable inductances of this type may be used for several purposes. Their most obvious application is to the calibration of ballistic galvanometers for magnetic testing; and I have found them of the greatest value for quickly adjusting a galvanometer circuit to read B directly for any given iron ring. I need not dwell on this application at present, but proceed to describe several methods to which they are applicable.

## 6. Measurement of Mutual Inductance (Method A).

Any unknown mutual inductance, whose value lies within the range of the variable standard, can be at once determined by connecting the primaries of the unknown and the variable in series to B (fig. 5), a source of alternating or intermittent



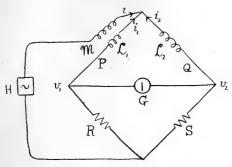
current, while the secondaries, with their windings in opposition, are connected in series to a vibration galvanometer G. The variable M is then adjusted to bring the deflexion to zero, and the reading gives directly the value of the unknown M. This is an extremely simple method as it involves no knowledge of any resistances. A ballistic galvanometer and a commutated current may be used. This method does not apply to mutual inductances higher than the maximum value of the variable standard; for these another method will be described below (see § 8).

# 7. Measurement of Self Inductance (Method B).

In fig. 6 let a variable mutual inductance M whose primary includes the subdivided coil be connected into a Wheatstone's network, as shown, along with a self inductance L<sub>2</sub>. Let the resistances of the arms be P, Q, R, and S respectively,

the self inductance of the arm P being  $L_1$  (the secondary coils of M) and that of Q being  $L_2$ . Let H be a source of periodic current and G a vibration galvanometer tuned to resonance with it, so that we may take the wave form of the

Fig. 6.



currents to be a sine curve. Let the instantaneous potentials of the three upper corners be  $v_1$ , 0, and  $v_2$  respectively, and the instantaneous values of the currents into the upper corner be  $i_1$ ,  $i_2$ , and i as marked. Let  $p=2\pi n$  where n is the frequency, and for convenience of writing let  $p\sqrt{-1}$  be denoted by  $\alpha$ , so that  $\alpha^2=-p^2$ . The mutual inductance M may be made positive or negative according to the way in which the coils are connected; and in all that follows we might write  $\pm$  M for M throughout. When the galvanometer shows a balance,  $v_1=v_2$ , and the instantaneous value of the current through G is zero.

Also

$$i = -i_1 - i_2$$

Accordingly we may write

$$(P+L_1\alpha)i_1-M\alpha i=(Q+L_2\alpha)i_2;$$

therefore

$$[P + (L_1 + M)\alpha]i_1 = [Q + (L_2 - M)\alpha]i_2$$

also

$$Ri_1 = Si_2$$
.

 $\mathbf{Hence}$ 

$$S[P+(L_1+M)\alpha]\!=\!R[\,Q+(L_2-M)\alpha].$$

Equating the real and imaginary parts each to zero we have

$$SP = QR$$
, . . . . . . (1)

and 
$$S(L_1+M) = R(L_2-M)$$
... \*(2)

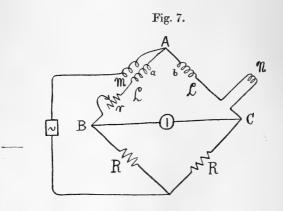
\* (Nov. 22, 1907) I find that a case slightly more complicated than that of Equation (2) has been worked out and applied in an ingenious manner by Grätz (Wied. Ann. vol. 50. p. 766, 1893).

Phil. Mag. S. 6. Vol. 15. No. 85. Jan. 1908.

Exactly the same equations hold when the positions of the source and the galvanometer are interchanged.

The most useful case is when the noninductive arms are made equal, i. e. S=R; then (1) and (2) become

This case gives an extremely convenient way of measuring small self inductances, which is done as follows.



The arrangement is shown in fig. 7. The noninductive arms are equal (R, R). In the arm AB there is the secondary coil a of self inductance L in series with a practically noninductive rheostat r. In the arm AC is placed a "balancing" coil b also of self inductance L and of resistance equal to or slightly greater than that of b. By adjusting r the bridge will balance when M=0. The small self inductance N to be measured is now inserted in series with coil b in arm AC, and a balance obtained by altering r and M. Then, by (3), N=2M. Thus N is found directly from the reading of M. and the range of values that can be measured runs from 0 up to twice the highest reading of the variable mutual inductance. For values of N above this range the more general case (equations (1) and (2)) may be used.] The L's of the coils a and b should be adjusted to equality once for all by putting M at zero and setting one of the coils. An exact setting is convenient, but not necessary, for if La and Lb differ slightly, they can be balanced (without N) by a small reading  $M_0$ . If

M be the reading for balance when N is inserted, then  $N = 2(M - M_0)^*$ .

Even if a and b are well matched, it is always well to begin

by reading their difference if any.

It will be noticed that the method is really a differential one; when N is introduced into the arm AC no alteration has to be made in the other arms except to increase the resistance of AB by an amount equal to the resistance of the coil N. But although it has all the advantages of differential measurement, the reading can be made to give N directly without having to take a difference at all. This is due to the use

of the inductive balancing coil  $b \uparrow$ .

The method has the advantage that it does not require the knowledge of the absolute value of any resistance. The non-inductive bridge arms must be equal; to check the equality they can be interchanged. For the noninductive adjustable resistance r I usually employ a special rheostat consisting of two slightly flattened thin wires running parallel to one another at a few millimetres distance, with a sliding contact piece across them to complete the circuit. The inductance of such a rheostat can be approximately calculated, and may thus be allowed for when measuring very small self inductances. The inductance of the part added to compensate for the introduction of N has merely to be subtracted from the result.

In practice the method proves very convenient; with the variable mutual inductance described above, self inductances of any value from 0·1 microhenry up to 2000 microhenries can be measured directly without the bridge being altered in any way except in the rheostat r. In a later model shown in the accompanying Plate IX. the whole scale of the movable coil corresponds to 20 microhenries, and at this value it can be read to 1 or 2 in 1000—at 200 microhenries to 1 or 2 in 10,000. All the resistances of the coils are very low, and the sensitivity can be considerably increased by using M. Wien's method of connecting the vibration galvanometer to the bridge by means of a transformer of suitable ratio  $(n_1/n_2$  small). The

Mag.' 2nd edit. vol. ii. § 756.

<sup>\* (</sup>Oct. 1st, 1907.) If, instead of the coil N, a condenser K with series (absorption) resistance q be added, then

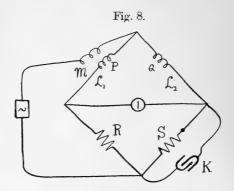
 $<sup>1/</sup>p^2K = 2M,$ 

and q=change in r.

† If coil b be made noninductive we revert to Maxwell's method of comparing the M of a pair of coils with the L of one of them. Equation (2) then reduces to L/M = -(1+R/S). Maxwell, 'Elect. &

method will also give the difference between two unknown self inductances introduced into AB and AC.

The addition of a condenser to Method (B) gives an interesting corroborative method (Method C). If (fig. 8) the condenser K is in shunt with S,



it may be shown that, for a balance,

Equation (7) gives a check of K against M without having to measure the frequency. The adjustment is dependent on p, however, and therefore a steady frequency is necessary, which is not required in Carey Foster's Method.

From (6) and (7) we get

$$Q(P-Q) = 2p^2M(L-M)$$
. (8)

8. Measurement of Mutual Inductance greater than Standard (Method D).

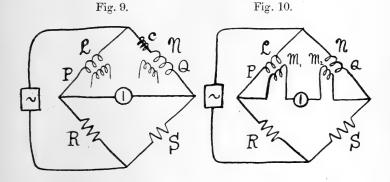
When the unknown M is beyond the range of the variable standard the following method is applicable.

Let the primaries of the variable standard and the unknown M be connected up as in fig. 9, adding to the latter if

necessary a coil c of sufficient self inductance to make N considerably greater than L. Let a balance be obtained (by Maxwell's Method) and hence

$$PS=RQ$$
, . . . . . . (9)

and NS=LR. . . . . . (10)



Now, without altering any other branches, let the secondary coils be introduced (in opposition) into the galvanometer circuit as shown in fig. 10.

If a balance be now obtained by adjusting the variable M, then it is easy to show that

$$(P+R)M_2 = (Q+S)M_1, . . . . (11)$$

and 
$$PS - p^2 M_2 (L - M_1) = QR - p^2 M_1 (N - M_2)$$
. (12)

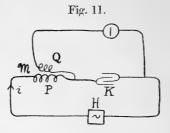
Since (9) and (10) still hold, these equations both reduce to

$$RM_2 = SM_1$$
 . . . . (13)

which gives  $M_2$  immediately in terms of the reading  $M_1$  and the resistances R and S (neither of which include copper coils). The self inductance of the added coil c need not be known, but if R and S have not a slide wire between them, c ought to be slightly adjustable, which is easily arranged by having part of it a small coil of a few turns that can be shifted about over the remainder.

## 9. Measurement of Capacities (Method E).

As in fig. 11, let the primary P of the variable standard be connected in series with a condenser K to a periodic



source H, while the secondary Q is connected to a vibration galvanometer as shown. Let M be adjusted until the galvanometer gives no deflexion, in which case we have

$$\pm M\alpha i = \frac{1}{K\alpha}i, \quad . \quad . \quad . \quad . \quad (14)$$
or
$$\pm p^2 MK = -1.$$

The secondary must be connected in such a direction that the lower sign is taken, and thus

$$p^{2}MK=1, \dots (15)$$

where M is in henries and K in farads.

It is interesting to notice that this formula is similar in form to that for resonance with a condenser and self inductance, viz.  $p^2LK=1$ . With self inductance we usually tune to get a maximum current through the galvanometer; with mutual inductance, on the other hand, we tune for zero current. If M is in henries and K in microfarads, equation (15) gives

$$n \doteq \frac{159.2}{\sqrt{\text{MK}}}, \quad . \quad . \quad . \quad . \quad (16)$$

and if M and K are known, the frequency can be determined. If the frequency is not fairly high, the product MK becomes inconveniently high, e. g. M=1 henry, K=10 mfds. gives  $n = 50 \sim$  per sec. In contrast, n = 10,000 for 256 microhenries and 1 mfd.

The following is a practical example of the method:—The source was a microphone hummer for 2000 ~ per sec. and the detecting instrument a tuned telephone. A balance was

obtained for  $K=10\cdot06$  mfds. and  $M=0\cdot626_6$  millihenry, whence the frequency was found to be  $2004\sim$  per sec. With another condenser (a carefully calibrated subdivided one), capacities of  $1\cdot000$ ,  $0\cdot900$ ,  $0\cdot800$ ,  $0\cdot701$ ,  $0\cdot601$ , and  $0\cdot551$  gave

$$n=1999, 2005, 2009, 2001, 2004, and 2001 \sim per sec.$$

respectively; the variable M was not, however, so accurately readable in this case.

In this method it is very important that the insulation resistance S of the condenser shall be high. If the leakage is not negligible, equation (14) becomes

$$\pm M\alpha i = \frac{S}{1 + SK\alpha}i$$

$$= \frac{S(1 - SK\alpha)}{1 + p^2S^2K^2}i. \qquad (17)$$

Putting the real part equal to zero we have

$$1/(1+p^2S^2K^2)=0$$
,

showing that an exact balance can only occur when  $p^2S^2K^2=\infty$ . In practice the insulation resistance of a good mica condenser is quite high enough to give a good balance; even a good paraffined paper condenser will work fairly well, but an ordinary one gives only a minimum deflexion on the galvanometer \*.

The application of this null method to the high frequencies used in wave telegraphy is made difficult by reason of the coexistence of two frequencies in the waves used.

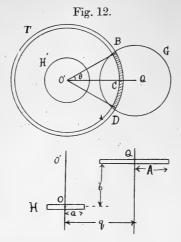
## APPENDIX.

Scale of Excentric-Coil Variable Mutual Inductance.

The problem of finding the mutual inductance between two circles (thin circular coils) not in the same plane and whose axes are parallel has not yet been solved, as far as I know. For any particular case the result may be calculated by quadratures as follows.

<sup>\*</sup> This may, however, be due more to absorption than leakage.

In fig. 12 let the two circles be H and G, of radii a and A respectively, b being the distance between their planes, and



q the distance between their axes. Let the circle H' be the projection of H on the plane of G, and let BCD be an elementary strip concentric with H' of radial width  $\partial r$ , where O'B = r. Let  $O'B = \theta$ . Then the M between circle H and strip BCD

$$= \frac{\theta}{\pi}. \text{ (M of circle H and annulus TBD)}$$

$$= \frac{\theta}{\pi}. \frac{\partial}{\partial r} \left[ -4\pi n_1 n_2 \sqrt{ar} \left\{ \left( k - \frac{2}{k} \right) F_1 + \frac{2}{k} E_1 \right\} 10^{-9} \right] \partial r,$$

or

$$\partial \mathbf{M} = \frac{\theta}{\pi} \cdot \frac{2\pi n_1 n_2 10^{-9}}{\sqrt{(a+r)^2 + b^2}} \left\{ 2a(\mathbf{F}_1 - \mathbf{E}_1) - (r-a) \left(\frac{k}{k'}\right)^2 \mathbf{E}_1 \right\} \partial \mathbf{r},$$
 where

$$k=2 \sqrt{ar} / \sqrt{(a+r)^2 + b^2} = \sin \gamma,$$
  

$$k' = \cos \gamma,$$

and  $\mathbf{F}_1$  and  $\mathbf{E}_1$  are complete elliptic integrals to modulus k.

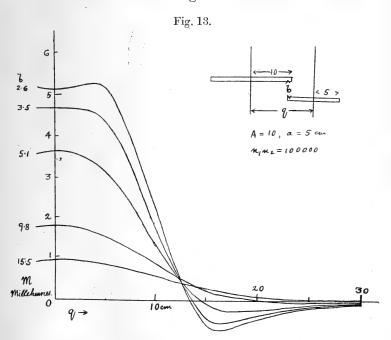
$$\theta = \cos^{-1} \frac{r^2 + q^2 - A}{2rq}.$$

Thus when a, A, b, and q are given, by calculating  $\partial M$  by (18) for a series of equally spaced successive values of r, from  $r=q \sim A$  to q+A, and adding in the usual way, the value of M can be approximately found. By this process

which is rather laborious, the following approximate values were found, when A=20, a=10, b=5 cm., and  $n_1$   $n_2=100,000:$ —

q.		м.
cm.	$\mathbf{n}$	illihenries.
0		9.3
5		9.7
10		$9 \cdot 9$
15		6.7

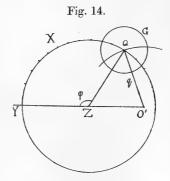
It is interesting to notice that the maximum value of M does not occur when the axes of the coils are coincident (q=0). To avoid the labour of the calculation by quadratures, some rough experiments were made with coils of finite section (about  $0.6 \times 0.6$  sq. cm.). From one set of these the series of curves shown in fig. 13 was obtained. The coils



were of mean radii A=10, a=5 cm. respectively,  $n_1$   $n_2$  being 100,000, and q and b were given various values. It will be seen that for b=2.6 the maximum M does not occur at the symmetrical position (just as in the case calculated above). For equal coils, however, the coaxial position gives

the maximum M. The curves also show that the value of q for which M vanishes and changes sign becomes greater and greater as the mean planes of the coils are set at greater distance from one another. The ratio of A/a has been made 2 in this example, as that is a suitable proportion for use in a practical instrument. Having now the curves connecting M with q, the distance between the axes of the two coils, it is easy to investigate the variety of angular scales obtainable by turning one of the coils round an axis parallel to its own axis.

Let a definite value of b be taken, say b=5, which is convenient in practice, and in fig. 14 let the smaller coil be



movable about an axis perpendicular to the plane of the paper at Z, and let the radius  $ZQ = \rho$ . Let the distance ZO' of the axis Z from O' (the point where the axis of the other coil cuts the plane of the paper) be h. Let the angular scale reading  $YZQ = \phi$ .

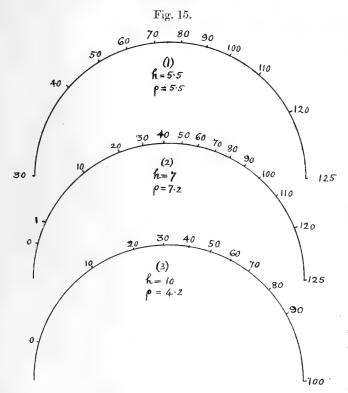
Then by choosing various values for  $\rho$  and h we can get a wide variety of movement of the centre Q (of the movable coil) relatively to O', and hence a variety of scale calibra-

tions. Since  $\cos \phi = \frac{q^2 - h^2 - \rho^2}{2h\rho}$ , the angle  $\phi$  corresponding

to a reading M can be got from q, h, and  $\rho$ . The scale can be most easily set off by the following geometrical construction. Draw a circle with centre Z and radius  $\rho$ , and make ZO' equal to h. Then find on the (b=5) curve in fig. 13 the q corresponding to a particular value of M. With this value of q as radius, a circle with centre O' will cut the circle X at the point of the scale required. By taking successive values of M the direct-reading scale can be set off round the circumference of the circle X.

As an example, in fig. 15 are given three scales for h=5.5,  $\rho=5.5$ ; h=7,  $\rho=7.2$ ; and h=10,  $\rho=4.2$  respectively, when A=10, a=5, b=5, and  $n_1$   $n_2 = 33,000$ .

Although these scales give very different ranges, the general characteristic of all three is an openness at both ends; no proportions that I have tried tend much to make the scale uniform throughout. The openness at the lower values is a distinct advantage, however, when dealing with



small inductances; but care must be taken, when marking that part of the scale, that the subdivisions shall be accurately marked and not put in merely by interpolation.

Scale (2) in fig. 15 is the best of the three and is nearly that which I have used in practice.

In conclusion I desire to express my best thanks to Dr. Glazebrook, for his kind encouragement and valued advice.

Sept 21, 1907.

XII. The Electron Theory of Matter and the Explanation of Magnetic Properties. By G. A. Schott, University College of Wales, Aberystwyth\*.

§ 1. TN a previous series of communications to this Journal it has been shown that spectrum-lines cannot be ascribed to the *free* vibrations of systems of electrons in orbital motion of atomic dimensions, partly because the intensities of most of the waves emitted are far too small to produce observable effects, partly because the wave-lengths of those waves, which are of sufficient intensity, are generally far too short. When we consider the experimental evidence in favour of the view that the atoms of a gas, which absorb and emit light, are only a small fraction of the whole number for instance the researches of Stark † and his associates in the canal-ray spectrum, the recent work of Pflüger ‡ on the absorption in a Geissler tube, and of Wick § on the fluorescence of resorufin,—we are led to the conclusion that spectrum lines are due to some special mechanism in the atom, which is set in operation during the act of ionization and operates only as long as the ion lasts, but is unaffected by disturbances which are sufficient only to produce free vibrations of the electrons of the atom without altering its structure.

Be this as it may, spectroscopic phenomena throw much less light on the structure of the *average* atom than has hitherto been supposed; we are thus driven to seek information from other sources, such as the phenomena of magnetism.

§ 2. It has been shown by Richarz || and R. Lang¶ that an electrolytic ion, revolving in an orbit of atomic dimensions with a period either greater or less than those of light-waves, is equivalent to a molecular magnet, whose moment is of the order of one twenty-fifth of the average moment of an atom of iron magnetized to saturation. We conclude that an atom built up of revolving electrons is capable of accounting for magnetic phenomena, provided a sufficiently large proportion of the atoms of the substance are effective.

More detailed investigations by Voigt \*\* and by J. J. Thomson ††, however, indicate a peculiar difficulty, in so far as they lead to the conclusion that an assemblage of mutually independent electrons, revolving in elliptic orbits, give on

<sup>\*</sup> Communicated by the Author.
† Stark, Drude Ann. xxi. p. 401.
† Pflüger, Ann. d. Phys. (4) xxiv. p. 515.
§ Wick, Phys. Ztschf. viii. p. 181.
|| Richarz, Wied. Ann. lii. p. 410.
¶ R. Lang, Drude Ann. ii. p. 483.
\*\* Voigt, Drude Ann. ix. p. 115.

<sup>††</sup> J. J. Thomson, Phil. Mag. [6] vi. p. 673.

the average no magnetic moment at all. If, however, the electrons are subjected to impulses irregularly distributed at comparatively long intervals, magnetic effects may be produced (Voigt); or if the electrons are subject to sufficiently rapid dissipation of energy, so that their orbits continually diminish in area, an average magnetic moment results and the system is paramagnetic (J. J. Thomson). hypothesis is quite satisfactory; for Voigt's hypothesis requires either very large numbers of independent electrons in the atom, or very powerful impulses, to produce an appreciable effect (§ 22), while that of J. J. Thomson requires very great dissipation of energy, and besides leaves little scope for accounting for diamagnetism (§ 22). As a matter of fact we shall see that neither hypothesis is necessary; for a system of electrons in orbital motion must group themselves in rings, if their radiation is to be sufficiently small for permanence; and a ring, as opposed to a system of independent electrons, possesses magnetic properties (§ 21).

§ 3. The magnetic effects to be explained may be con-

veniently grouped as follows:-

(1) Effects due to the mutual interaction of the molecules of the substance; these are usually taken to include hysteresis and coercive force, and the numerous interactions between strain and magnetization. It should, however, be borne in mind that some of these effects, such as the variation of magnetic susceptibility with magnetic force, can be explained without intermolecular action (Theory of Stefan\* and W. Siemens†).

(2) Effects due to the actions between the atoms of the molecule. The smallness of the magnetism of oxides and salts of iron and cobalt in proportion to the amounts of iron,

or cobalt, contained in them, is an effect of this kind.

(3) Effects due to the constitution of the atom itself. The fact that the amalgams of iron and cobalt studied by Nagaoka ‡ are as strongly magnetic, in proportion to their concentration, as the pure metals, coupled with the usual supposition, made on chemical grounds, that the molecule of a metal is monatomic, can hardly be explained except by supposing that magnetism is, in the last resort, an atomic property; and that the largeness of the magnetism of iron and its congeners is due to some peculiarity of atomic structure. This conclusion is supported by the experiments of St. Meyer § and others, from which it results that atomic magnetism is a periodic

† Nagaoka, *Wied. Ann.* lix. p. 66. § St. Meyer, *Wied. Ann.* lxviii. p. 325; lxix. p. 236

<sup>\*</sup> Stefan, Wien. Ber. lxix. (2) p. 165; Wiedemann, Elektrizität, iii.

<sup>†</sup> W. Siemens, Wied. Ann. xxiv. p. 113.

function of the atomic weight and is in some very close connexion with the atomic volume. In fact iron and its congeners do not occupy a quite exceptional position amongst the elements; for instance, Meyer finds that erbium in

 $Eb_2O_3$  is four times as magnetic as iron in  $Fe_2O_3$ .

In view of these facts we shall in what follows restrict ourselves to the explanation of atomic magnetism; nevertheless the results have an immediate bearing on the magnetic properties of amalgams and powders of iron and its congeners for small concentrations, and generally of elementary substances, which are weakly paramagnetic or diamagnetic. The problem then is this:—How far can an atom, built up of coaxal rings of revolving electrons, be made to account for the magnetic properties of elementary substances, without the use of additional hypotheses, such as that of external impulses (Voigt), or that of great dissipation of energy (J. J. Thomson)?

§ 4. Let us consider a ring of n electrons, which, when undisturbed, revolve in a circle of radius  $\rho$  with uniform angular velocity  $\omega$ . A controlling field is presupposed of such a kind that the steady motion is stable; and the velocity is supposed to be such that it is practically permanent in spite of radiation. Let c be the velocity of light; write  $\beta = \omega \rho/c$ . We can assign a limit to  $\beta$  for any given value of n, which must not be exceeded if the ring is to have the

necessary degree of permanence.

The equations of steady motion are

$$\frac{e^2 \rho}{e^2} m \beta^2 = \frac{\rho^2}{e^2} P - (1 + \beta^2) K + V ; \qquad . \qquad . \qquad . \qquad (2)$$

where m is the transverse mass of the electron, e its charge in electrostatic units, P the central force of the controlling field, and K, U, V functions of n and  $\beta$  given by the equations

$$\begin{split} \mathbf{K} &= \sum_{i=1}^{i=n-1} \frac{1}{4} \operatorname{cosec} \frac{\pi i}{n}, \\ \mathbf{U} &= 2 \sum_{i=1}^{s=\infty} \left[ s n \beta^2 \mathbf{J'}_{2sn} \left( 2 s n \beta \right) - s^2 n^2 (1 - \beta^2) \int_0^{\beta} \mathbf{J}_{2sn} \left( 2 s n x \right) dx \right], \\ \mathbf{V} &= \sum_{s=0}^{s=\infty} \left( s + \frac{1}{2} \right) \operatorname{cot} \frac{(2s+1)\pi}{2n} \left[ \beta (1 - \beta^2) \mathbf{J}_{2s+1} \{ (2s+1)\beta \} \right. \\ &\qquad \qquad + (1 + \beta^2) \int_0^{\beta} \mathbf{J}_{2s+1} \{ (2s+1)x \} dx \right]^*. \\ &\quad \quad * \operatorname{Schott}, \operatorname{Phil}, \operatorname{Msg}, \left[ 6 \right] \operatorname{xii}, \operatorname{pp}, 22/23. \end{split}$$

Equation (1) enables us to assign the upper limit to  $\beta$  (vide table \*): for instance, we might admit a secular change in the wave-length of the D lines, and therefore of  $\beta$ , of not more than, let us say, six ten-thousandths of an Angström unit in thirty years, that is,  $10^{-16}$  of its value per second; or an equivalent change in m, both leading to value of  $\beta$  of the same order.

§ 5. The controlling field may be partly due to other rings of moving negative electrons, but is mainly due to positive charges of such amount as to make the whole system neutral except when ionized. The positive charge may be distributed throughout the atom (J. J. Thomson's model), or may be concentrated in discrete charges (Nagaoka's model). In any case the steady part of the field must be symmetrical about the axis of the ring, and derivable from a potential  $\Phi$ ; and the part of  $\Phi$  due to any ring can be calculated as if all the charges of the ring were uniformly distributed along it and revolving with it. In addition the disturbing ring produces periodic forces, the fundamental frequency of which is the difference between the angular velocities of that ring and the one under investigation. These forces excite perturbations and cause additional radiation; they must be small enough not to upset the permanence and stability of the system. The necessary conditions being supposed satisfied, the periodic forces need trouble us no further. Thus we may write

$$P = \frac{\partial \Phi}{\partial \rho}. \qquad (3)$$

§ 6. At a large distance the ring is equivalent to:—

(1) a charge ne at the centre;

(2) a polarized element of electric moment  $\mathbf{p} = \sum e\mathbf{r}$ ;

(3) a magnetized element of magnetic moment

$$\mathbf{m} = \frac{1}{2} \sum_{e} e \left[ \mathbf{r} \, \frac{\mathbf{v}}{e} \right].$$

r is the vector from the centre to the *i*th electron of the ring, v is its velocity relative to the centre, and  $\Sigma$  denotes summation for *i* from 0 to n-1.

When the centre of the ring is in motion with velocity **w** the polarized element (2) is itself equivalent to a magnet of moment  $\frac{1}{2} \left[ \mathbf{p} \frac{\mathbf{w}}{e} \right] \dagger$ . The translatory motion of the atom as **a** whole may be neglected, even in the case of a gas at high

\* Loc. cit. p. 24.

<sup>†</sup> H.A. Lorentz, Math. Encyclopaedie, V. 14, §§ 12-15.

temperature, since its velocity is exceedingly small in comparison with c, the velocity of light. Hence  $\mathbf{w}$  may be taken to mean the velocity of the centre of the ring relative to its position in the undisturbed atom.

§ 7. Let the axis of the undisturbed ring be Oz; the azimuth of the *i*th electron may be written in the form  $\omega t + \delta + \frac{2\pi i}{n}$ , where  $\delta$  is an arbitrary angle; its coordinates (x, y, z), referred to axes fixed in the plane of the ring, are

$$x = \rho \cos\left(\omega t + \delta + \frac{2\pi i}{n}\right), \quad y = \rho \sin\left(\omega t + \delta + \frac{2\pi i}{n}\right), \quad z = 0.$$
 (4)

When the ring is disturbed these coordinates are increased by terms of the form

where  $\xi$ ,  $\eta$ ,  $\zeta$  are the components of the displacement, supposed small and measured from the position that the electron would have occupied at the same time, if it had not been disturbed from steady motion. They may be expressed as the sums of functions of the type

$$Ae^{-\kappa t}\cos\left(qt-k\frac{2\pi i}{n}+\alpha\right),$$

where k is an integer between  $\pm \frac{n}{2}$ , such that the number of nodes, and also of loops, in the disturbed ring is 2k. q is the frequency relative to the rotating ring,  $q + k\omega$  that relative to an outside observer.

§ 8. The particular type of disturbance we have to consider is that due to a constant external magnetic force  $\mathbf{h}$ , which we shall suppose makes an angle  $\theta$  with the axis of the undisturbed ring, the axis being drawn to correspond to a right-handed rotation. We shall choose the arbitrary angle  $\alpha$  so that  $\mathbf{h}$  lies in the plane of xz; then the components of  $\mathbf{h}$  are  $(h \sin \theta, 0, h \cos \theta)$ . Assuming the usual expression for the mechanical force on a moving charge as given by the Maxwell-Lorentz theory, we find for the components of the force on the *i*th electron in the directions of the tangent,

inward radius and axis, the values

$$\left(0, -\beta eh \cos \theta, -\beta eh \sin \theta \cos \left(\omega t + \delta + \frac{2\pi i}{n}\right)\right).$$
 (6)

Since the disturbances produced are of the same types as the disturbing forces, with the same frequencies and damping, but, it may be, displaced in phase, we have only to consider two types of disturbance:-

(1) A disturbance due to the radial force  $-\beta eh \cos \theta$ . q, kare both zero;  $\xi$ ,  $\eta$ ,  $\zeta$  are constant and the same for

each electron of the ring.

(2) A disturbance due to the axial force

$$-\beta eh\sin\theta\cos\left(\omega t + \delta + \frac{2\pi i}{n}\right), \quad q = \omega, \quad k = -1.$$

In each case we have  $q + k\omega = 0$ , that is, the disturbance, like the force, is stationary for an outside observer. Nevertheless it is periodic relative to the electrons of the ring, and like any other forced vibration may exhibit phenomena of resonance. This is a very important fact; from it follows as a consequence that a ring of revolving electrons may, and actually does, possess magnetic properties much greater than would be the case if its electrons were all independent.

Further, it follows from the stationary character of the disturbance with reference to space, expressed by the equation  $q + k\omega = 0$ , that the radiation of energy into space is exceedingly small, in fact only of the same order as the radiation due to the steady motion; hence the displacement in phase is almost zero, which means that the maximum of the disturbance lies very nearly in the plane through the axis and the magnetic force.

 $\S$  9. By means of the expressions of  $\S$  6 and the equations (4)-(6) we find the following expressions for the electric and magnetic moments of the whole ring, on the supposition that squares and products of the displacements may be

neglected:—

(a) Steady motion.

(b) Disturbance due to the axial magnetic force, and therefore radial mechanical force  $(-\beta eh \cos \theta)$ .

$$\delta \mathbf{p}_{1} = ne(0, 0, \zeta), \ \delta \dot{\mathbf{p}}_{1} = ne(0, 0, \dot{\zeta}) = 0$$

$$\delta \mathbf{m}_{1} = \frac{1}{2}ne(0, 0, \delta(\beta \rho)$$

$$(8)$$

It must not be forgotten that this force not merely displaces the ring but also changes its velocity.

Phil. Mag. S. 6. Vol. 15. No. 85. Jan. 1908.

(c) Disturbance due to the radial magnetic force, and therefore axial mechanical force

$$\left(-\beta eh\sin\theta\cos\left(\omega t + \delta + \frac{2\pi i}{n}\right)\right)$$
.

$$\delta \mathbf{p}_{2} = \frac{1}{2} ne(\mathbf{A}' - \mathbf{B}, \mathbf{A} + \mathbf{B}', 0), \quad \delta \dot{\mathbf{p}}_{2} = \frac{1}{2} ne\omega(\mathbf{A}, \mathbf{A}', 0) \\
\delta \mathbf{m}_{2} = \frac{1}{2} ne\beta(-\mathbf{C}, -\mathbf{C}', 0) \quad . \quad . \quad . \quad , \quad . \quad .$$
(9)

where we have written

$$(\xi, \eta, \zeta) = (A, B, C) \cos\left(\omega t + \delta + \frac{2\pi i}{n}\right) + (A', B', C') \sin\left(\omega t + \delta + \frac{2\pi i}{n}\right).$$

§ 10. The varying electric moment  $\delta \mathbf{p}_2$  in (e) gives rise to a magnetic force  $rot\left(\frac{\delta \dot{\mathbf{p}}_2}{er}\right)$ ; its components are linear func-

tions of the direction cosines of the radius vector **r** with respect to axes fixed in the ring, and therefore their values vanish on the average for a large number of rings, whose axes are distributed equally in all directions, and for a distant point.

The electric moment  $\delta \mathbf{p}$  gives rise to a magnetic moment  $\frac{1}{2} \left[ \delta \mathbf{p} \frac{\mathbf{w}}{e} \right]$ , where for  $\mathbf{w}$  we may take the velocity of the centre of the ring relative to its undisturbed position (§ 6); but this velocity, as well as  $\delta \mathbf{p}$  itself, is small of the order of the disturbance, so that the resulting magnetic moment is of

the second order and may be neglected.

Thus we need not consider the polarization in finding the

magnetic field due to the disturbing ring.

The magnetic moment in the steady motion by (a) gives a component in the direction h equal to  $\frac{1}{2}ne\beta\rho\cos\theta$ ; since this must vanish on the average the mean value of  $\cos\theta$  vanishes, as it must do for rings equally distributed.

It only remains to consider the moments  $\delta m$  given by (8) and (9); by the principle of superposition of small disturbances we may find the effect of each separately, and add them

together to find the total effect.

§ 11. To find the effect of (8) it is necessary to consider the motion of the ring during the variable period accompanying the establishment of the magnetic field h. Since the motion of the ring itself is periodic, the simplest method of proceeding is to resolve the mechanical force into simple harmonic components, either by Fourier's series, or integrals, and to determine the corresponding forced vibrations, and thence, by summation, the resulting motion.

Suppose the variable period to extend from t=0 to  $t=\tau$ ;

then we may write, between these limits,

$$h = \sum_{s=-\infty}^{s=\infty} H_s \text{ exp. } \iota \frac{2\pi st}{\tau}, \qquad (10)$$

where the coefficients are small for large values of s, and the series may be supposed differentiable. The axial magnetic force, which alone concerns us here, is got by multiplying by  $\cos \theta$ , and gives rise to a mechanical force to the centre  $-\beta eh \cos \theta$  (§ 8, (6)). Since however the magnetic force is changing, an induced electric force E is produced along the circle, which causes a tangential mechanical force eE. To find it we apply Faraday's Law of Induction to the circuit made up of the orbit of the electron from t=0 to  $t=\tau$ , together with so much of a circle and radius as are necessary to make a closed circuit. This circuit differs from the original circular orbit, described an integral number of times, by quantities of the order of the disturbance; since it occurs on both sides of the equation with h, or E, as a factor we may substitute the circle for it without making an error of more than the second order. Thus we get, from the general equation of Maxwell's theory,

$$\mathbf{E} = -\frac{\rho}{2c} \frac{d}{dt} (h \cos \theta). \quad . \quad . \quad . \quad (11)$$

§ 12. A great simplification ensues because we may generally suppose  $\tau$  very large compared with the time of revolution of an electron. In fact  $\tau$  will rarely be as small as  $10^{-6}$  second—the value for a coil of radius 1 cm., length 100 cm., with 1000 turns and of resistance 10 ohm would be about  $4.10^{-5}$  sec.—while the period for an electron describing an orbit of atomic dimensions with a velocity one thousandth of that of light is about  $2.10^{-15}$  sec. Since such a velocity is already very small to be consistent with stability for a ring of more than 3 electrons (in J. J. Thomson's well-known model the lower limit is in general several hundredths of the velocity of light), our assumption appears to be amply justifiable on experimental and theoretical grounds for any but the smallest rings.

Hence if q be the frequency of any one of the harmonic components of the disturbance,  $\frac{q}{\omega}$  and  $\hat{a}$  fortion  $\frac{q\beta}{\omega}$ , is an exceedingly small quantity.

We shall now develope the equations of the disturbed motion; as the full investigation is long it will not be possible to do more than indicate the method. We first use the equations of motion of an electron under any forces \* to get

<sup>\*</sup> Abraham, Elektrizität, vol. ii. p. 123.

the equations for an electron slightly disturbed from uniform circular motion. Next we calculate the changes in the forces exerted by the controlling field, which are due to the displacement of the given electron from its position in steady motion, and, when necessary, those due to displacements of neighbouring rings. Lastly, we calculate the changes in the forces exerted by the remaining electrons of the ring. The last problem is the most troublesome when the velocity of the ring is not small.

§ 13. With the notation of § 7 the equations for the

disturbance  $(\xi, \eta, \zeta)$ , whether periodic or not, are

$$\begin{split} &-\frac{2e^{2}\beta^{3}}{3\rho^{3}(1-\beta^{2})^{2}}\frac{\ddot{\xi}}{\omega^{3}} + \mu\ddot{\xi} + \left\{\frac{2e^{2}\beta^{3}(3+\beta^{2})}{3\rho^{3}(1-\beta^{2})^{3}} + \mu\omega\frac{\dot{m}}{m}\right\}\frac{\dot{\xi}}{\omega} \\ &+ \frac{2e^{2}\beta^{3}}{\rho^{3}(1-\beta^{2})^{2}}\frac{\ddot{\eta}}{\omega^{2}} - (\mu+m)\omega\dot{\eta} - \left\{\frac{2e\beta^{3}(1+3\beta^{2})}{3\rho^{3}(1-\beta^{2})^{3}} + \mu\omega\frac{\dot{m}}{m}\right\}\eta = \delta T. \\ &- \frac{2e^{2}\beta^{3}}{\rho^{3}(1-\beta^{2})^{2}}\frac{\ddot{\xi}}{\omega^{2}} + (\mu+m)\omega\dot{\xi} \\ &- \frac{2e^{2}\beta^{3}}{3\rho^{3}(1-\beta^{2})}\frac{\ddot{\eta}}{\omega^{3}} + m\ddot{\eta} + \left\{\frac{2e^{2}\beta^{3}(3+\beta^{2})}{3\rho^{3}(1-\beta^{2})^{2}} + \mu\omega\frac{\dot{m}}{m}\right\}\frac{\dot{\eta}}{\omega} - \mu\omega^{2}\eta = \delta P. \\ &- \frac{2e^{2}\beta^{3}}{\mathcal{E}\rho^{3}(1-\beta^{2})}\frac{\ddot{\zeta}}{\omega^{3}} + m\ddot{\zeta} + \left\{\frac{2e^{2}\beta^{5}}{3\rho^{3}(1-\beta^{2})^{2}} + \mu\omega\frac{\dot{m}}{m}\right\}\frac{\dot{\xi}}{\omega} = \delta S. \quad . \quad . \quad . \end{split}$$

(12)

m is the transverse mass as before, in which a small secular change is admitted as possible for the sake of generality;  $\mu$  is the longitudinal mass and is given by  $\mu = \frac{d(m\beta)}{d\beta}$ 

δP, δS are the components of the disturbing force due to all causes. The electron is supposed to be slightly disturbed from steady motion in a circle of radius  $\rho$  with angular velocity  $\omega$ .

§ 14. If the controlling field be due to fixed charges, the

changes in the forces  $P = \frac{\partial \Phi}{\partial \rho}$ ,  $S = -\frac{\partial \Phi}{\partial z}$ (this being zero

in the steady motion) are due to the displacement  $(\xi, \eta, \zeta)$ of the electron, which is also its displacement relative to the controlling field. Since the field is symmetrical about the axis of the ring, the component displacement along the ring,  $\xi$ , produces no change, and for the same reason no force is produced along the ring itself. A force of this latter type would be produced by induction if the charges producing the field themselves moved.

For shortness write

$$R = \frac{\partial^2 \Phi}{\partial \rho^2}, \quad S = \frac{\partial^2 \Phi}{\partial \rho \partial z}, \quad T = \frac{\partial^2 \Phi}{\partial z^2}.$$

Then the variations of the component forces due to the displacement relative to the controlling field are

$$\delta T = 0, \qquad . \qquad . \qquad . \qquad .$$

$$\delta P = -R\eta + S\zeta, \qquad . \qquad . \qquad .$$

$$\delta S = S\eta - T\zeta. \qquad . \qquad . \qquad . \qquad .$$

$$(13)$$

The new symbols R, S, T, which are usual ones for second differential coefficients, will cause no confusion, for in the steady motion the force components, which would be denoted by S, T, both vanish.

When the field is due to a central positive charge (Nagaoka), or to a sphere of uniform positive electrification (J. J. Thom-

son), S vanishes, but in general this is not the case.

§ 15. For periodic disturbances the forces on the *i*th electron due to the rest of the ring are given by the following equations:—

where K, U, V have the same meanings as before (§ 4), and

$$\mathbf{H} = \sum_{i=1}^{i=n-1} \frac{1}{4} \csc \frac{\pi i}{n} \sin^2 \frac{k \pi i}{n}, \quad \mathbf{M} = \sum_{i=1}^{i=n-1} \frac{1}{8} \cot \frac{\pi i}{n} \csc \frac{\pi i}{n} \sin \frac{2k \pi i}{n},$$

$$\mathbf{N} = \sum_{i=1}^{i=n-1} \left( \frac{1}{2} \csc^3 \frac{\pi i}{n} - \frac{1}{4} \csc^2 \frac{\pi i}{n} \right) \sin^2 \frac{k\pi i}{n},$$

$$\mathbf{W} = \sum_{s=0}^{s=\infty} \left( s + \frac{1}{2} \right) \cot \frac{(2s+1)\pi}{2n} \left[ \beta \mathbf{J}_{2s+1} \left\{ (2s+1)\beta \right\} - \int_{0}^{\beta} \mathbf{J}_{2s+1} \left\{ (2s+1)x \right\} dx \right].$$

A, A, ... are functions of  $\beta$ , q, and k defined by the equations

$$\begin{split} \mathbf{A} &= n \sum_{j=-\infty}^{j=\infty} a \left\{ 2k + 2jn, \quad \left( 2k + 2jn + \frac{2q}{\omega} \right) \beta \right\}, \\ A &= \sum_{s=-\infty}^{s=\infty} \cot \frac{(2s+1)\pi}{2n} a \left\{ 2k + 2s + 1, \left( 2k + 2s + 1 + \frac{2q}{\omega} \right) \beta \right\}, \end{split}$$

with similar expressions for B, B, C, C, D, D, where

$$\begin{split} a\left(m,\,l\beta\right) &= \frac{l^2\beta^2}{4}\, \mathsf{J}_m'(l\beta) - \frac{m^2 - l^2\beta^2}{8}\, l\!\int_0^\beta \mathsf{J}_m(lx) dx. \qquad . \qquad . \\ b\left(m,\,l\beta\right) &= \frac{m - l\beta^2}{8}\, l\beta \mathsf{J}_m(l\beta) + \frac{m + l\beta^2}{8}\, l\int_0^\beta \mathsf{J}_m(lx) dx. \qquad . \\ c\left(m,\,l\beta\right) &= \frac{1 - \beta^2}{16}\, l^2\beta^2 \mathsf{J}_m'(l\beta) + \frac{3 + \beta^2}{16}\, l\beta \mathsf{J}_m(l\beta) \\ &\quad + \frac{(1 + \beta^2)(m^2 + l^2\beta^2) - 4ml\beta^2 - 3 - \beta^2}{16}\, l\int_0^\beta \mathsf{J}_m(lx) dx. \end{split}$$

$$d\left(m,\,l\beta\right) &= -\frac{1 - \beta^2}{16}\, l^2\beta^2 \mathsf{J}_m'(l\beta) + \frac{1 + 3\beta^2}{16}\, l\beta \mathsf{J}_m(l\beta) \\ &\quad + \frac{(1 + \beta^2)(m^2 + l^2\beta^2) - 4ml\beta^2 - 1 - 3\beta^2}{16}\, l\int_0^\beta \mathsf{J}_m(lx) dx. \end{split}$$

 $A_0, A_0, \dots$  are the values of  $A, A, \dots$  in the particular case when k=0 and q=0.

The expressions (14) and (15) remain true for a complex frequency, q, corresponding to finite damping.

§ 16. The functions  $a, \ldots$  all vanish when the argument  $l\beta$  vanishes. When  $l\beta$  is not zero, they diminish rapidly as the order m increases.

In the particular case of vibrations stationary in space, for which  $q + k\omega$  vanishes, as in our present problem, we have

(15)

m=l+2k, while in A... we have l=2jn, and in A... l=2s+1. The terms in A... corresponding to j=0 vanish, and the largest terms left are those corresponding to  $j=\pm 1$ , which are of the orders  $m=\pm 2n+2k$ , and very small. We may neglect A..., as well as the quantities  $B_0$ , U; this only amounts to neglecting the radiation, which in the present case is of the same order of smallness as the steady motion radiation from the ring. For the same reason we shall neglect the small terms involving the variation of mass,  $\dot{m}$ , of the electron in equations (12).

A second simplification occurs in any case of periodic motion, whether damped or not, and therefore also in the present problem. The terms due to radiation on the left-hand sides of equations (12), that is, those involving  $\frac{e^2}{\rho^3}$  as a factor, are easily seen to cancel, term by term, corresponding terms on the right-hand sides of equations (14). Hence in (12) we have only to take into account the following terms:

$$\mu \ddot{\xi} - (\mu + m)\omega \dot{\eta}, \quad (\mu + m)\omega \dot{\xi} + m \ddot{\eta} - \mu \omega^2 \eta, \quad m \ddot{\zeta}. \quad (16)$$

on the left-hand sides; while on the right-hand sides of (14) we need only take into account the real parts of the factors of  $\xi$  and  $\iota\eta$  in the first, of  $\iota\xi$  and  $\eta$  in the second, and of  $\zeta$  in the third equation.

§ 17. We shall now apply our results to our first problem, the calculation of the part of  $\delta \mathbf{m}$  due to induction, that is, to the axial magnetic force  $h\cos\theta$ , which produces the radial mechanical force  $-\beta eh\cos\theta$  (6), and while it is changing,

the tangential induced force  $e\mathbf{E} = -\frac{e\rho}{2c}\frac{d}{dt}(h\cos\theta)$  (11).

When everything has become steady,  $\delta \mathbf{m}_1 = (0, 0, \frac{1}{2}ne\delta(\beta\rho))$  (§ 9. (b) (8)). Now we have

$$\delta\beta = \frac{\dot{\xi}}{c}, \quad \delta\rho = -\eta, \quad \text{whence } \delta\left(\beta\rho\right) = \beta\left(\frac{\dot{\xi}}{\omega} - \eta\right).$$
Hence
$$\delta \mathbf{m}_{1} = \frac{1}{2}ne\,\beta\left(\frac{\dot{\xi}}{\omega} - \eta\right) \text{ along Oz.} \qquad . \qquad . \qquad (17)$$

This equation shows that, although the variations of the field are comparatively slow, nevertheless  $\frac{\dot{\xi}}{\omega}$  is of the same order of magnitude as  $\eta$  and  $\zeta$ .

In the present case we have k=0; hence by § 15, H=M=N=0.

Further,  $\frac{q\beta}{\omega}$  is a very small quantity (§ 12). It follows from equations (15) that  $A-A_0$ ,  $C-C_0$ ,  $D-D_0$  can be expanded in ascending even powers of  $\frac{q\beta}{\omega}$ , beginning with the second, while B can be expanded in odd powers, beginning with the first. Bearing this in mind, we see that on the right-hand sides of (14) the coefficient of  $\xi$  is of the order  $\left(\frac{q\beta}{\omega}\right)^2$  and that of  $\eta$  of the order  $\frac{q\beta}{\omega}$  in the first equation, that of  $\xi$  of order  $\frac{q\beta}{\omega}$  and those of  $\eta$  and  $\zeta$  of order zero in the remaining equations. Now  $q^2\xi = -\xi$ ,  $\iota q\eta = \dot{\eta}$ ,  $\iota q\xi = \dot{\xi}$ ; hence we retain the terms of the first order, that is, of order  $\dot{\xi}$  and  $\dot{\eta}$  in the first equation, and those of zero order, that is, of order  $\dot{\xi}$ ,  $\eta$  and  $\zeta$  in the others.

Thus we write  $A - A_0 = \frac{1}{2} A_0'' \left(\frac{2q\beta}{\omega}\right)^2$ ,  $B = B_0' \frac{2q\beta}{\omega}$ , and neglect  $C - C_0$ ,  $D - D_0$ , where the dash denotes differentiation with respect to the argument in  $A_0$  and  $B_0$ . By help of (15) we easily find

 $2\beta A_0^{\prime\prime} = \frac{dV}{d\beta}, \quad 2B_0^{\prime} = \frac{dV}{d\beta} + \beta W, \quad . \quad . \quad (18)$ 

where V, W are the series already defined (§§ 4, 15).

§ 18. Collecting our results together and using (6), (11), (12) ... (18), we get the following equations of vibration:—

$$\frac{i}{\xi} \left\{ \mu + \frac{e^{2}}{\rho^{3}\omega^{2}} \left( 2K\beta^{2} - \beta \frac{dV}{d\beta} \right) \right\} - i \left\{ (\mu + m)\omega + \frac{e^{2}}{\rho^{3}\omega} \left( 2K\beta^{2} - \beta \frac{dV}{d\beta} \right) \right\} \\
= -\frac{e\rho}{2c} \frac{d}{dt} (h\cos\theta). \qquad (19)$$

$$\dot{\xi} \left\{ (\mu + m)\omega + \frac{e^{2}}{\rho^{3}\omega} \left( 2K\beta^{2} - \beta \frac{dV}{d\beta} \right) \right\} + \eta \left\{ R - \mu\omega^{2} + \frac{e^{2}}{\rho^{3}} \left( 2K - 2V + \beta \frac{dV}{d\beta} \right) \right\} \\
- \zeta S = -\beta eh\cos\theta. \qquad (19)$$

 $\eta S - \xi T$  = 0. . . . . .

We integrate the first equation, substitute from it in the second, and eliminate  $\zeta$  by means of the third. In the result we use the equation of steady motion (2) and obtain the equations

$$\begin{split} \left(\frac{\dot{\xi}}{\omega} - \eta\right) \left\{ \mu \omega^2 + \frac{e^2}{\rho^3} \left( 2K\beta^2 - \beta \frac{dV}{d\beta} \right) \right\} - m\omega^2 \eta &= -\frac{1}{2}\beta e h \cos \theta \\ \left(\frac{\dot{\xi}}{\omega} - \eta\right) m\omega^2 + \eta \left( R - \frac{S^2}{T} + \frac{2P}{\rho} \right) &= -\frac{1}{2}\beta e h \cos \theta. \end{split}$$

These give

$$\frac{\xi}{\omega} - \eta = -\frac{1}{2}\beta eh \cos\theta \frac{m\omega^2 + R - \frac{S^2}{T} + \frac{2P}{\rho}}{m^2\omega^4 + \left(R - \frac{S^2}{T} + \frac{2P}{\rho}\right)\left\{\mu\omega^2 + \frac{e^2}{\rho^3}\left(2K\beta^2 - \beta\frac{dV}{d\beta}\right)\right\}}.$$

The component of the resulting increase in moment in the direction of h is  $\delta m_1 \cos \theta = \frac{1}{2} ne \beta \cos \theta \left(\frac{\dot{\xi}}{\omega} - \eta\right)$ , by (17). Substituting the value of  $\frac{\dot{\xi}}{\omega} - \eta$ , and averaging for all rings of an element of the substance, we find for the mean effective moment per ring due to axial magnetic force

$$\delta \overline{\mathbf{m}}_{1} = -h \frac{ne^{2}\rho^{2}}{12c^{2}m} \frac{m\omega^{2} + R - \frac{S^{2}}{T} + \frac{2P}{\rho}}{m\omega^{2} + \left(R - \frac{S^{2}}{T} + \frac{2P}{\rho}\right) \left\{\frac{\mu}{m} + \frac{e^{2}}{c^{2}m\rho}\left(2K - \frac{1}{\beta}\frac{dV}{d\beta}\right)\right\}} \cdot (20)$$

§ 19. We shall now use our equations to determine the part of the moment due to the radial magnetic force, which produces the axial mechanical force

$$-\beta eh\sin\theta\cos\left(\omega t + \delta + \frac{2\pi i}{n}\right) \quad (\S \ 8 \ (6)).$$

The increase in the moment is given in  $\S 9 (c) (9)$ , and is equal to

$$\delta \mathbf{m}_2 = \frac{1}{2} ne \boldsymbol{\beta} (-C, -C', 0),$$

where 
$$\zeta = C \cos \left(\omega t + \delta + \frac{2\pi i}{n}\right) + C' \sin \left(\omega t + \delta + \frac{2\pi i}{n}\right)$$
.

Thus we need calculate only the axial displacement  $\zeta$ . In the present case we have k=-1,  $q=\omega$ , so that as before  $q+k\omega=0$ . We find by § 15

$$H = \frac{1}{4} \cot \frac{\pi}{2n}$$
,  $M = H - K$ ,  $N = 2K - H$ . (21)

It follows from equations (15), by using the continuation formulæ for Bessel Functions, that in the present case

$$A - A_{0} = \frac{1}{\beta} \frac{dV}{d\beta} - \frac{2V}{\beta^{2}} - \frac{2(1 - \beta^{2})W}{\beta^{2}}, \quad B = A - A_{0} + V + \beta^{2}W.$$

$$C - C_{0} = A - A_{0} - \beta \frac{dV}{d\beta} + 3V, \quad D - D_{0} = V. \qquad (22)$$

Remembering that the radiation terms disappear as before, we must take account of the following terms on the right-hand sides of (14), because of (21) and (22):—

$$\begin{split} -\frac{\xi[2\mathbf{K}-(1-\beta^2)\mathbf{H}+A-A_0]-\iota\eta[(1-\beta^2)(\mathbf{K}-\mathbf{H})+\mathbf{V}+A-A_0],}{\iota\xi[(1-\beta^2)(\mathbf{K}-\mathbf{H})+\mathbf{V}+A-A_0]-\eta\Big[(1-\beta^2)\mathbf{K}-\frac{2-5\beta^2-\beta^4}{2}\mathbf{H}\\ &+\mathbf{V}+A-A_0\Big],}\\ \xi\Big[(1+\beta^2)\mathbf{K}-\frac{\beta^2(3+\beta^2)}{2}\mathbf{H}-\mathbf{V}\Big] \end{split}$$

respectively.

Substituting these results in (12), together with (13) and (16), we get the equations of vibration in the form

$$\begin{split} -\xi \big[\mu\omega^2 - \frac{e^3}{\rho^3} \big\{ 2\mathbf{K} - (1-\beta^2)\mathbf{H} + A - A_0 \big\} \big] \\ -\iota\eta \big[ (\mu + m)\omega^2 - \frac{e^2}{\rho^3} \big\{ (1-\beta^2)(\mathbf{K} - \mathbf{H}) + \mathbf{V} + A - A_0 \big\} \big] = 0 \\ \iota\xi \big[ (\mu + m)\omega^2 - \frac{e^3}{\rho^3} \big\{ (1-\beta^2)(\mathbf{K} - \mathbf{H}) + \mathbf{V} + A - A_0 \big\} \big] \\ + \eta \left[ \mathbf{R} - (\mu + m)\omega^2 + \frac{e^2}{\rho^3} \left\{ (1-\beta^2)\mathbf{K} - \frac{2-5\beta^2 - \beta^4}{2}\mathbf{H} + \mathbf{V} + A - A_0 \right\} \right] - \zeta \mathbf{S} = 0 \\ -\eta \mathbf{S} + \zeta \left[ \mathbf{T} - m\omega^2 - \frac{e^2}{\rho^3} \left\{ (1+\beta^2)\mathbf{K} - \frac{\beta^2(3+\beta^2)}{2}\mathbf{H} - \mathbf{V} \right\} \right] \\ = -\beta e h \sin\theta \exp. \iota \left( \omega t + \delta + \frac{2\pi i}{n} \right) \end{split}$$

since the disturbing force is axial and equal to the real part of  $-\beta eh \sin \theta \exp \iota \left(\omega t + \delta + \frac{2\pi i}{n}\right)$ , § 8 (6).

Write

$$Q = \mu \omega^2 - \frac{e^2}{\rho^3} \{ (1 - \beta^2)(K - H) + V + A - A_0 \}, \qquad (23)$$

and use the equation (2),  $m\omega^2 = \frac{P}{\rho} - \frac{e^2}{\rho^3} \{(1 + \beta^2)K - V\};$ 

we get

$$\begin{aligned} & \mathbf{P}(\mathbf{i}\boldsymbol{\xi} - \boldsymbol{\eta})\mathbf{Q} + \boldsymbol{\eta}\frac{\mathbf{P}}{\rho} = 0, \\ & (\mathbf{i}\boldsymbol{\xi} - \boldsymbol{\eta})\left(\mathbf{Q} + \frac{\mathbf{P}}{\rho}\right) + \boldsymbol{\eta}\left\{\mathbf{R} + \frac{e^2}{\rho^3}\frac{\beta^2(3+\beta^2)}{2}\mathbf{H}\right\} - \zeta\mathbf{S} = 0, \\ & \mathbf{\eta}\mathbf{S} + \zeta\left\{\mathbf{T} - \frac{\mathbf{P}}{\rho} + \frac{e^2}{\rho^3}\frac{\beta^2(3+\beta^2)}{2}\mathbf{H}\right\} = -\beta e \ h \sin \theta \exp \ \iota(\omega t + \delta + \frac{2\pi i}{n}). \end{aligned} \right\}$$

From these equations it follows at once that

$$\begin{split} \mathbf{C}' = & \mathbf{0}, \\ \mathbf{C} = & -\frac{\beta e h \sin \theta}{\mathbf{T} - \frac{\mathbf{P}}{\rho} + \frac{e^2}{\rho^3} \frac{\beta^2 (3 + \beta^2)}{2} \mathbf{H} - \frac{\mathbf{S}^2}{\mathbf{Q} \left\{ \mathbf{R} + \frac{\mathbf{P}}{\rho} + \frac{e^2}{\rho^3} \frac{\beta^2 (3 + \beta^2)}{2} \right\}} + \frac{\mathbf{P}^2}{\rho^2} \end{split}$$

Since the corresponding moment is equal to  $-\frac{1}{2}ne\beta C$  and is along the axis of x, we get the effective moment of the ring by multiplying by  $\sin \theta$ . Averaging the result for all values of  $\theta$ , we get for the mean effective moment due to the radial magnetic force the expression

$$\mathbf{m_2} = h \frac{1}{\mathbf{T} - \frac{\mathbf{P}}{\rho} + \frac{e^2}{\rho^3} \frac{\beta^2 (3 + \beta^2)}{2} \mathbf{H} - \frac{\frac{1}{3} n e^2 \beta^2}{\mathbf{Q} \left\{ \mathbf{R} + \frac{\mathbf{P}}{\rho} + \frac{e^2}{\rho^3} \frac{\beta^2 (3 + \beta^2)}{2} \mathbf{H} \right\} + \frac{\mathbf{P}^2}{\rho^2}}.$$
 (25)

§ 20. The total mean effective moment per ring is equal to  $\overline{\delta \mathbf{m}} = \overline{\delta \mathbf{m}}_1 + \overline{\delta \mathbf{m}}_2$ ; since all these quantities are proportional to h, at any rate for small displacements, we introduce the

specific moments, defined by equations such as  $p = \frac{\delta \mathbf{m}}{h}$ .

If N be the number of rings per unit volume, the magnetic susceptibility is given by k = Np, if the several rings do not act upon each other; this is at any rate an approximation for small concentrations, such as we find in amalgams of iron and cobalt.

In order to form some idea as to the performance of our expressions (20) and (25) we shall consider some special arrangements of rings, without enquiring into their stability and permanence.

(1) Single ring with a fixed positive charge at the centre (type of Nagaoka).

Let the positive charge be numerically equal to ve. Then

$$\Phi = -\frac{ve^2}{\sqrt{\rho^2 + z^2}}.$$

Steady motion requires  $\frac{\partial \Phi}{\partial z} = 0$ , i. e. z = 0; hence

$$P = \frac{\nu e^2}{\rho^2}$$
,  $R = -\frac{2\nu e^2}{\rho^3}$ ,  $S = 0$ ,  $T = \frac{\nu e^2}{\rho^3}$ .

Since  $H = \frac{1}{4} \cot \frac{\pi}{2n}$  in (25) by (21), we get, from (20) and (25),

$$p_{1} = -\frac{ne^{2}\rho^{2}}{12c^{2}m},$$

$$p_{2} = \frac{8n\rho^{3}}{3(3+\beta^{2})}\tan\frac{\pi}{2n}.$$
(26)

(2) Single ring inside a fixed positive sphere of uniform density (type of J. J. Thomson).

Let the positive charge be numerically equal to  $\nu e$ , and the radius of the sphere b. Then

$$\Phi = -\frac{3\nu e^2}{2b} \left(1 - \frac{\rho^2 + z^2}{3b^2}\right).$$

Steady motion requires z=0; hence

$$P = \frac{\nu e^2 \rho}{b^3}, R = \frac{\nu e^2}{b^3}, S = 0, T = \frac{\nu e^2}{b^3}.$$

These give

$$p_{1} = -\frac{ne^{2}\rho^{2}}{12c^{2}m} \frac{m\omega^{2} + \frac{3\nu e^{2}}{b^{3}}}{m\omega^{2} + \frac{3\nu e^{2}}{b^{3}} \left\{ \frac{\mu}{m} + \frac{e^{2}}{c^{2}m\rho} \left( 2K - \frac{1}{\beta} \frac{dV}{d\beta} \right) \right\}}$$

$$p_{2} = \frac{8n\rho^{3}}{3(3+\beta^{2})} \tan \frac{\pi}{2n} . \qquad (27)$$

§ 21. We shall now calculate the value of k given by (26) or (27) for the weakest iron amalgam (0·19 per cent.) studied by Nagaoka \*, on the assumption that each atom contains a single ring of n electrons of the type considered in § 20 (1)

<sup>\*</sup> Nagaoka, Wied. Ann. lix. p. 66.

and (2), the atoms being independent. For this particular amalgam the magnetization curve is practically a straight line up to  $H=3200~\mathrm{C.G.S.}$  so that the condition of independence is satisfied; hence we may put h=H.

Let  $\rho = x \cdot 10^{-8}$  cm., where  $10^{-8}$  cm. is the conventional radius of the atom. We at once find from the second

equation of (26), or (27) that

$$1.8.10^{-24}.x^3 > p_2 > 1.05.10^{-24}.x^3$$

for when n=2,  $\tan \frac{\pi}{2n} = 1$ , while  $\beta^2$  is very small, and when  $n=\infty$ , limit  $n \tan \frac{\pi}{2n} = \frac{\pi}{2}$ , while  $\beta^2$  is nearly unity.

The ratio  $p_1/p_2$  is of the order  $\frac{na}{2\pi\rho}$ , where a is the radius of the electron, given by  $a=\frac{3e^2}{5e^2m}$ . Since  $2\pi\rho/n$  is the distance between consecutive electrons,  $\frac{na}{2\pi\rho}$  is small, and  $p_1/p_2$  negligible.

A·19 per cent. iron amalgam contains ·025 gr. iron per c. c.; taking the mass of the hydrogen atom to be 1·1. 10<sup>-24</sup> gr. we

find  $N=4.10^{20}$ . Hence since k=Np

$$0007.x^3 > k > 0004.x^3$$
.

Nagaoka's curve gives k = 0013.

We see that an atom containing only a single ring of radius  $10^{-8}$  cm., for which x=1, gives a value of from one half to one quarter of the experimental value of k. An atom containing from two to four independent rings, or one slightly larger ring, could account for the actual atomic magnetism of iron; since, however, the rings could not be independent, the above investigation will not apply. Before proceeding to the study of systems of rings, it will be convenient to consider the performance of the formulæ of Voigt and Thomson already referred to.

§ 22. Voigt considers a medium containing a large number of independent electrons describing elliptic orbits and subject to damping, the irregular stationary state being maintained by subjecting each electron to periodic shocks which renew its energy. Let  $\psi$  be the mean kinetic energy of an electron, and  $\phi_1$  its mean potential energy,  $\psi_1$  its mean kinetic energy just after a shock. Voigt's formula (51) ( $l.\ c.\ p.\ 128$ ) is in

our notation equivalent to the following:

$$p = \frac{e^2 \rho^2}{12c^2 m} \frac{\phi_1 - \psi_1}{\psi} \quad . \quad . \quad . \quad (28)$$

for a single electron.

We notice at once that np is precisely of the order of  $p_1$ , as given by (26) or (27), unless  $\frac{\phi_1 - \psi_1}{\psi}$  be very large.

On account of damping  $\psi_1$  is probably many times  $\psi$ , but  $\phi_1$  is of the order  $\psi$ , unless we suppose the potential energy to be much increased by the shock. This, however, can hardly be the case, since a shock does not instantaneously change the position of the electron, but merely its velocity. It follows that while (28) can account for a much larger diamagnetic moment than is actually found, it can hardly account for a sufficiently large paramagnetic moment.

Voigt gives a formula (134) (l. c. p. 134) for the magnetic moment due to rotating electrons, which is equivalent to

$$p = -\frac{e^2 k^2}{4c^2 m} \quad . \quad . \quad . \quad (29)$$

for a single electron, where k is the radius of gyration, and for simplicity the densities of both electric charge and mass have been supposed uniform. If we assume the mass to be

wholly electromagnetic, so that 
$$m = \frac{3e^2}{5c^2a}$$
, while  $k^2 = \frac{a^2}{5}$ , we get  $p = -\frac{a^3}{12}$ .

The moment due to a negative electron is thus far too small to account even for diamagnetism; but that due to a rotating positive sphere of atomic radius would, with the same assumption as to its mass, give a diamagnetic moment comparable with the paramagnetic moment due to a ring as given by (26) or (27). This will be of importance to us in § 23.

A third formula (103) (l. c. p. 143) may be written

$$m = \frac{ek^2}{2c} \left( \overline{h_0} - \frac{eh}{2cm} \right), \quad . \quad . \quad . \quad (30)$$

where k is the radius of gyration of a rotating electron and  $\overline{h_0}$  its mean initial angular velocity of rotation. The formula gives the mean magnetic moment due to an assemblage of rotating electrons, whose rotation round the axis of symmetry is unresisted, whilst that about other axes is strongly resisted, the stationary state being supposed to have been reached. Apart from theoretical difficulties due to the term  $\overline{h_0}$ , this term is not sufficiently well defined to render the formula amenable to calculation, so that a comparison with experiment is impossible.

Lastly, J. J. Thomson gives a formula (1) (l. c. p. 689), equivalent to

$$p = -\frac{e^2}{4c^2m} \epsilon^{-\kappa t} \int_0^t \epsilon^{\kappa t} \frac{d}{dt} \left( \rho^2 \right) . \, dt,$$

where the motion of the electron in its orbit is supposed to be resisted by a force equal to  $m\kappa$  times the velocity. In consequence  $\rho$  is supposed to diminish. To obtain definite results integrate by parts, and let  $\rho_0$  be the initial value of  $\rho$ ; we get

$$p = \frac{4c^2m}{e^2} \left\{ \rho_0^2 \epsilon^{-\kappa t} - \rho^2 + \kappa \epsilon^{-\kappa t} \int_0^t \epsilon^{\kappa t} \rho^2 dt \right\} < \frac{e^2}{4c^2m} (\rho_0^2 - \rho^2), (31)$$

since  $\rho^2 < \rho_0^2$  in the integral.

This result shows that the paramagnetism due to dissipation of energy from the moving electron is at most of the

order of magnitude of  $p_1$ , as given by (26) or (27).

From this discussion we conclude that the formulæ (28) and (30), although from their *form* capable of accounting for the paramagnetism of iron, can be regarded as little more than empirical; because the very terms, which make them

capable of doing so, the factor  $\frac{\phi_1 - \psi_1}{\psi}$  in (28), and the term  $\overline{h_0}$ 

in (30), are too ill-defined to serve as the basis for numerical calculations. On the other hand, the formulæ (29) and (31), which are free from theoretical objections, will only account for diamagnetism. The formulæ (26) and (27) again can account for the paramagnetism of iron, but cannot explain diamagnetism, because the term  $p_1$ , which gives diamagnetism, is far too small to counteract the term  $p_2$ , which gives paramagnetism; thus these formulæ, although successful to the extent of accounting for the paramagnetism of iron, and therefore superior to the others hitherto proposed, are incomplete. The remedy has been already indicated in the remarks made respecting (29): the paramagnetic moment  $p_2$ can be balanced, in whole or part, by the diamagnetic moment due to a charged sphere of either sign and of atomic dimensions, set in motion by the induction set up in starting the magnetic field.

§ 23. We are thus led to consider the following system:—
(3) A single ring of negative electrons inside a rigid, but free, positive sphere of uniform density (type of J. J. Thomson).

It is not difficult to prove that the tilting of the ring due to the radial magnetic force produces no couple tending to rotate the sphere; this couple is due entirely to the inductive effect of the changing field at starting, which is partly external, partly due to the changes in radius and velocity of the ring studied in § 18 and represented by equations of the type (19).

It is not difficult to see that the part of the couple due to the ring bears to the part directly due to the external field a ratio, which is of the same order of smallness as the ratio  $p_1:p_2$  in § 20. The corresponding parts of the magnetic field due to the sphere bear to each other a ratio of the same degree of smallness, and therefore also do the resulting parts of the magnetic moment of the sphere. The large part we shall find to be of the order  $p_2$ , the small part of the order  $p_1$ ; the latter we shall neglect.

For the same reason we neglect the moment  $p_1$ , and the change in it due to the reaction of the sphere; and, in estimating the change produced in  $p_2$  by the sphere, we take into account only the rotation due to the external field. This

we shall now consider.

Let  ${\bf L}$  be the resulting couple, and  $\Omega$  the corresponding angular velocity; then

$$\dot{\Omega} = \frac{\mathbf{L}}{1},$$

where I is the moment of inertia of the sphere.

Divide the sphere into elementary rings with the diameter parallel to the external magnetic force h as axis; let dV be the volume of a ring,  $\rho'$  its radius,  $\epsilon$  the uniform electric density, and e' the charge of the sphere. The induced electric force E acts along the ring and is by Faraday's Law

given by  $2\pi\rho' \mathbf{E} = -\frac{1}{c} \frac{d}{dt} (\pi \rho'^2 h)$ , so that  $\mathbf{E} = -\frac{\rho'}{2c} \dot{h}$ . Hence also

$$\mathbf{L} = \int \mathbf{E} \rho' \epsilon d\mathbf{V} = -\frac{\epsilon \dot{h}}{2c} \int \rho'^2 d\mathbf{V} = -\frac{e'b^2}{5c} \dot{h},$$
and
$$\Omega = -\frac{e'b^2}{5c\mathbf{I}} \mathbf{h}, \qquad (32)$$

the sphere being supposed at rest in the absence of an external field.

§ 24. We shall now study the field due to the sphere. In the first place, the external field is the same as that due to an infinitely small magnet at the centre, whose moment is given by

$$m_3 = \frac{e'b^2}{5c}\Omega = -\frac{e'^2b^4}{25c^2I}h.$$

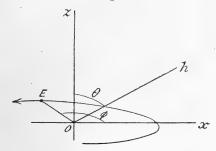
Hence the sphere has a specific moment given by

$$p_3 = -\frac{e'^2b^4}{25c^2\Gamma} \quad . \quad . \quad . \quad . \quad . \quad (33)$$

which is diamagnetic and in general of the order of magnitude of  $p_2$ .

§ 25. In the diagram E is the position of the *i*th electron of the ring at time t; its azimuth is  $\phi = \omega t + \delta + \frac{2\pi i}{n}$ . The direction of the external field, **h**, which by (32) is also that of  $\Omega$ , lies in the plane xOz, and makes the angle  $\theta$  with Oz.

Fig. 1.



The component angular velocities of the sphere therefore are  $\Omega \cos \theta$  along Oz, and  $\Omega \sin \theta$  along Ox. Since we require only the change in  $p_2$  we require only that component of the magnetic force due to the sphere, which gives an axial mechanical force, that is, we require only the radial magnetic force. Since the angle between the radius OE and the angular velocity  $\Omega \sin \theta$  is  $\phi$ , while  $\Omega \cos \theta$  is perpendicular to OE, the outward radial magnetic force is entirely due to  $\Omega \sin \theta$  and is equal to

$$\frac{e'}{cb} \left( 1 - \frac{3\rho^2}{5b^2} \right) \Omega \sin \theta \cos \phi *.$$

Therefore the axial mechanical force is the real part of

$$+\frac{e'^2b}{5c^2\mathrm{I}}\left(1-\frac{3\rho^2}{5b^2}\right)\beta\ eh\sin\theta\ \exp.\ \iota\left(\omega t+\delta+\frac{2\pi i}{n}\right). \eqno(34)$$

It must be added to the right-hand side of the third of equations (24) and is of the opposite sign, as is to be expected from Lenz's Law.

\* A. H. Bucherer, *Phys. Ztsch.* vol. vi. p. 269. *Phil. Mag.* S. 6. Vol. 15. No. 85. *Jan.* 1908.

§ 26. Proceeding as in § 19, we put  $P = \frac{\nu e^2 \rho}{b^3}$ ,  $T = \frac{\nu e^2}{b^3}$  S = 0, and  $e'^2 = \nu^2 e^2$ , and by (34) obtain

$$p_{2} = \left\{ 1 - \frac{v^{2}e^{2}b}{5c^{2}I} \left( 1 - \frac{3\rho^{2}}{5b^{2}} \right) \right\} \frac{8n\rho^{3}}{3(3+\beta^{2})} \tan \frac{\pi}{2n}. \quad (35)$$

The resulting moment of the system is  $p=p_2+p_3$ ; hence by (33) and (35) we get

$$p = -\frac{\nu^2 e^2 b^4}{25 c^2 \Gamma} + \left\{ 1 - \frac{\nu^2 e^2 b}{5 c^2 \Gamma} \left( 1 - \frac{3 \rho^2}{5 b^2} \right) \right\} \frac{8 n \rho^3}{3 (3 + \beta^2)} \tan \frac{\pi}{2n} (36)$$

The greatest value of p is given by putting  $I=\infty$ , when it reduces to  $p_2$  as given by (27); as I diminishes p diminishes also; when I takes its least value,  $\frac{6v^2e^2b}{25c^2}$ , corresponding to purely electromagnetic inertia, we have

$$p = \frac{b^3}{6} \left\{ \left( 1 + \frac{3\rho^2}{b^2} \right) \frac{\rho^3}{b^3} \frac{8n}{3(3+\beta^2)} \tan \frac{\pi}{2n} - 1 \right\}. \quad (37)$$

When  $\rho=0$  the expression (36) is obviously negative; when  $\rho=b$  it reduces to

$$-\frac{v^2e^2b^4}{25c^2I} + \left\{ 1 - \frac{2v^2e^2b}{25c^2I} \right\} \frac{8nb^3}{3(3+\beta^2)} \tan \frac{\pi}{2n}, \quad . \quad (38)$$

which is certainly positive because  $\frac{8n}{3(3+\beta^2)}$  tan  $\frac{\pi}{2n} > \frac{\pi}{3} > 1$ , and  $\frac{v^2e^2b^4}{25c^21} < \frac{b^3}{6}$ . Similarly  $\frac{dp}{do}$  is positive between these

limits; hence p vanishes once, and only once, as p increases from zero to its greatest value b. This means that for a sphere of given mass and radius, and for a ring of a given number of electrons and given velocity, there is a critical radius, such that the system is paramagnetic when the radius of its ring is larger, and diamagnetic when smaller. Thus the system of a sphere and a single ring can account qualitatively for both paramagnetism and diamagnetism.

§ 27. The magnetic moment is represented by the curves in fig. 2, which correspond to the four limiting cases:—

I. A sphere of infinite mass, and a ring of two, practically very few electrons;  $\frac{v^2e^2b}{25c^2l} = 0$ ,  $\frac{8n}{3+\beta^2} \tan \frac{\pi}{2n} = \frac{16}{9}$ .

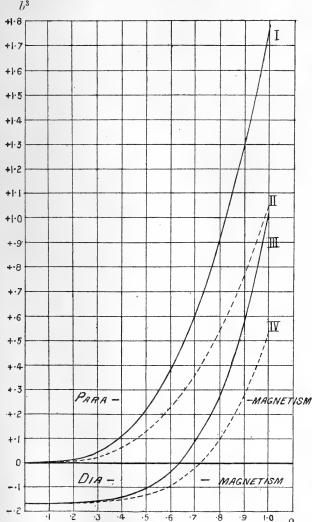
Fig. 2.—Curve for specific moment of Sphere and Ring.

II. Fixed sphere, few electrons.
II. Fixed sphere, many electrons.

| Mass of sphere infinitely great.

III. Movable sphere, few electrons
IV. Movable sphere, many electrons. | Mass of sphere purely electromagnetic.





II. A sphere of infinite mass, and a ring of an infinite, practically a large, number of electrons;

$$\frac{8n}{3+\beta^2}\tan\frac{\pi}{2n}=\pi.$$

III. A sphere whose mass is purely electromagnetic, that is equal to  $\frac{3\nu^2e^2}{5c^2b}$ , and a ring of few electrons;

$$\frac{v^2 e^2 b}{25c^2 1} = \frac{1}{6}.$$

IV. A sphere whose mass is purely electromagnetic, and a ring of many electrons.

The following conclusions can be drawn from these curves:—

(1) In similar sytems both paramagnetism and diamagnetism, as measured by the specific moment, are proportional to the volume.

(2) Increasing the mass of the sphere increases paramagnetism, and diminishes the critical radius.

- (3) Increasing the radius of the ring increases paramagnetism.
- (4) Increasing the number of electrons in the ring diminishes paramagnetism and increases the critical radius.

§ 28. We must now study the numerical values of the moments given by our formulæ and compare them with the values found by experiment. For this purpose it is most convenient to use the atomic susceptibilities of the elements; St. Meyer \* gives a table referred to one gram atom per litre with a unit for k equal to  $10^{-6}$ . If we take  $10^{-24}$  gr. to be the mass of the atom of hydrogen, we find the number of atoms in one c.c. of a solution or powder containing one gram per litre to be  $10^{21}$ ; hence we must multiply Meyer's numbers by  $10^{-27}$ .

Again, the weak iron amalgam studied by Nagaoka (§ 21) contained  $4.10^{20}$  atoms per c.c. and had a susceptibility 0013. This gives  $p=3\cdot2\cdot10^{-24}$  for iron. Meyer's table gives  $p=-2\cdot0\cdot10^{-28}$  for bismuth; all other elements have intermediate values with the possible exception of erbium, which Meyer estimates to be four times as magnetic as iron when pure, corresponding to  $p=1\cdot3\cdot10^{-23}$ . The greatest para-

magnetic moment thus is 16,000, perhaps 65,000, times as great as the greatest diamagnetic moment. The curves give the extreme values  $1.8 cdots b^3$  and  $-0.17 cdots b^3$ , in the ratio 10:1.

By taking b a few times the conventional atomic radius,  $10^{-8}$  cm. (or by choosing several rings) the greatest paramagnetic moment can easily be brought within the range of the system, which so far is quite satisfactory. We cannot, however, explain diamagnetism so easily, although the margin available is very large, for the diagram shows that our single ring system cannot possibly be diamagnetic unless the radius of the ring is less than the critical radius, the greatest value of which is 0.72.b.

Now  $\frac{\rho}{b}$  cannot be chosen at will, because the equation of steady motion (2) must be satisfied. In the present case of a neutral system we have  $\nu = n$ ,  $P = \frac{ne^2}{b^3}\rho$ ; thus (2) becomes

$$\frac{\rho^3}{b^3} - \frac{c^2 b}{e^2} \frac{m\beta^2}{n} \frac{\rho}{b} - \frac{(1+\beta^2)K - V}{n} = 0. \quad . \quad (39)$$

The last term is positive; in fact K is slightly greater than  $\frac{n}{2\pi} \log n$ , and in the series V  $J_{2s+1}\{(2s+1)\beta\}$  is positive, because  $\beta < 1$ , and  $(s+\frac{1}{2}) \cot \frac{(2s+1)\pi}{2n} < \frac{n}{\pi}$ ; putting in this value for the cotangent, we get a series whose value is equal to  $\frac{n}{2\pi} \{\beta^2 - (1+\beta^2) \log \sqrt{1-\beta^2}\}$ . Hence

$$\frac{(1+\beta^2)K - V}{n} > \frac{1+\beta^2}{2\pi} \{ \log (n\sqrt{1-\beta^2}) - \beta^2 \} > 0$$

for all values of  $\beta$  which are actually possible with radiation small enough for permanence.

Substituting the value  $\frac{\rho}{b} = 0.72$  in (39), we find

$$\log n < 2 \pi \frac{\rho^3}{b^3} < 2.0, n < 8,$$

on the assumption that  $\beta^2$  is negligibly small, which is certainly true for such small values of n. Hence we conclude that no single ring system can be diamagnetic unless the number of electrons is less than 8.

This number obviously does not give sufficient margin to account for the large number of diamagnetic elements known,

even if there were no other objections. Hence it becomes necessary to examine systems with more than one ring.

§ 29. The effect of the presence of other rings besides the one considered is twofold: -(1) Each ring contributes a term to the resultant specific moment of the system, so that the second terms in (36) and (38) must be replaced by sums of terms, one for each ring. (2) Each ring modifies the controlling field of every other ring, partly on account of its own steady motion, partly on account of its disturbance; the result is that the quantities  $T - \frac{P}{\rho}$ , S and R in equations (24) and (25) are altered. In particular  $T - \frac{P}{\rho}$ , which is zero in our models, becomes negative, and the rings become linked together. In consequence the total moment due to all the rings is by no means the sum of the moments they would contribute if independent of each other. When the linking is very loose the total moment is paramagnetic, but less than the sum of the separate moments, possibly less than that of a single ring; so that it may very well happen that the resulting moment of the system of sphere and rings is negative for certain arrangements of rings. The problem is, however, too complicated to be pursued further here, but it does suggest that magnetic properties are functions of the structure of the atom, depending on the number and arrangement of its electrons, just as directly as do the atomic weight and atomic volume.

## XIII. Note on the Focometry of a Concave Lens. By J. A. Tomkins, A.R.C.Sc. (Lond.)\*.

In a recent number of the Philosophical Magazine  $\uparrow$  Prof. Anderson described a simple method for the determination of the focal length of a concave lens in which f is calculated from observed values of u and v.

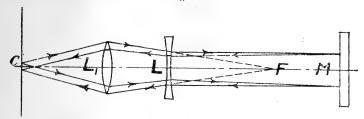
The following methods, in which the focal length of a concave lens is measured directly, occurred to the writer after reading Prof. Anderson's article. They correspond to two well-known methods which are employed in the case of a convex lens. They do not appear, however, to have been previously described.

I. Light from the cross-wires C (fig. 1) of an optical bench is brought to a focus at F by means of a convex lens L<sub>1</sub>. The concave lens L is then placed in the position shown and

<sup>\*</sup> Communicated by the Author. † Phil, Mag. June 1906.

adjusted until the rays reflected by the plane mirror M, passing through the lenses again, form an image of the cross-wires on the screen carrying them.

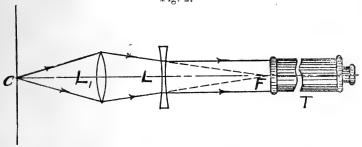
Fig. 1.



F is then at the principal focus of L and the distance between L and F is the focal length.

II. As in the first method, light from the cross-wires C (fig. 2) is brought to a focus at F. The concave lens L is

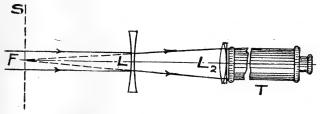




then inserted and adjusted until an image of the cross-wires is formed in the focal plane of the telescope T, which has been previously focussed for parallel rays. The distance between L and F is the focal length as before.

III. In this method a distant object is viewed through the concave lens L by means of the telescope T (fig. 3). The

Fig. 3.



latter will therefore be focussed as for an object at F, the principal focus of L.

To find the position of F, the lens L is removed and a screen S is adjusted until an image of it is formed in the focal plane of the telescope T. As in the previous methods, the focal length required is the distance between L and F.

In this experiment an auxiliary convex lens L<sub>2</sub> may be employed, if necessary, so that F may be brought to within a

short distance of the telescope.

Of these methods II. and III. appear to be more accurate than I.

Technical College, Bradford. Oct. 1907.

## XIV. Notices respecting New Books.

Recherches sur les Propriétés Optiques des Solutions et des Corps Dissous. Par M. C. CHÉNEVEAU. Paris: Gauthier-Villars. 1907. Pp. 190.

THIS memoir forms the thesis presented by the author for his Doctorate to the University of Paris. It contains the results of numerous determinations of the refractive index and dispersive power of various solutions (aqueous and others), and the conclusions deduced by the author from the results of his experiments. The apparatus employed by him consisted of a modified form of Féry refractometer. It is interesting to note that according to the author's researches there is little to choose between the law of Gladstone and that of Lorentz, although the latter appears to give rather more accurate results when dispersion is taken into account. Students of physical optics will find a great deal to interest them in this valuable contribution to our knowledge of the optical properties of solutions.

Rivista di Scienza. Anno I (1907), No. 1. Bologna: Nicola Zanichelli. 1907. Pp. 192.

The first issue of this new periodical, which is described as an "International Review of Scientific Synthesis," contains the following articles:—"La mécanique classique et ses approximations successives," by É. Picard; "Zur modernen Energetik," by W. Ostwald; "Problemi di chimica organica," by G. Ciamician; "Il concetto di specie in biologia," by F. Raffaele; "Die natürliche Zuchtwahl," by H. E. Ziegler; "Il carattere delle leggi economiche," by C. Supino; "Impartiality in History," by W. Cunningham; "Questions pédagogiques," by J. Tannery. In addition to these, there are reviews (in Italian) of various scientific works, and of recent progress in various departments of science. The scope of the new periodical, it will be seen, is

very wide, and from the list of future contributors it appears that the editors have been successful in securing the cooperation of many distinguished men of science from many lands, each of whom writes in his own language. We wish this high-class international publication every success, and hope that it will be instrumental in counteracting some of the evils which arise from over-specialisation.

Solubilities of Inorganic and Organic Substances. By A. Seidell, Ph.D. New York: D. Van Nostrand Co. London: Crosby Lockwood & Son. 1907. Pp. 368,

This important work of reference may be regarded as taking the place of Professor A. M. Comey's 'Dictionary of Chemical Solubilities,' published in 1894. Its compilation must have involved a very large amount of labour, and chemists will feel grateful to the author for the care and devotion which he has brought to bear on his somewhat formidable task. The substances are arranged in alphabetical order, and in addition an excellent index is provided at the end of the book. Great care has evidently been taken by the author to select the most reliable data in cases where a number of determinations was available. In warmly commending this useful work to the attention of chemists and physicists, we should like to draw their attention to the following extract from the author's Preface:—"A glance through the pages of this book will show the incompleteness of the data for many of the most common chemical compounds. Furthermore, many of the results given are of doubtful accuracy, although the best available. It is hoped, therefore, that a realisation of the present incomplete state of our information concerning solubilities as evidenced in these pages will stimulate investigations of many of those substances which have hitherto been studied iucompletely or not at all."

# XV. Proceedings of Learned Societies.

#### GEOLOGICAL SOCIETY.

[Continued from vol. xiv. p. 787.]

November 6th, 1907.—Sir Archibald Geikie, K.C.B., D.C.L., Sc.D., Sec.R.S., President, in the Chair.

THE following communications were read:-

- 1. 'On a Collection of Fossil Plants from South Africa.' By Prof. Albert Charles Seward, M.A., F.R.S., F.G.S.
- 2. 'Permo-Carboniferous Plants from Vereeniging (South Africa).' By Prof. Albert Charles Seward, M.A., F.R.S., F.G.S., and Thomas Nicholas Leslie, F.G.S.
- 3. 'On the Structure and Relations of the Laurentian System of Canada.' By Prof. Frank Dawson Adams, D.Sc., F.R.S., F.G.S.

This paper contains an outline of the results of the examination by Dr. Barlow and the author of an area of 4200 square miles, *Phil. Mag.* Sr. 6. Vol. 15. No. 85. *Jan.* 1908.

comprised within the Haliburton and Bancroft sheets of the Ontario & Quebec series of maps. The paper opens with a short account of Logan's work in the original Laurentian area. The main conclusions reached by the author may be thus summarized:—(1) The Laurentian System of Sir William Logan consists of a very ancient series of sedimentary strata, largely limestones, invaded by great volumes of granite in the form of bathyliths; (2) This sedimentary series is one of the most important developments of the pre-Cambrian rocks in North America, it presents the greatest body of pre-Cambrian limestones on the continent, and it is best designated as the Grenville Series; (3) The invading masses of granite are of enormous extent: they possess a more or less distinct gneissose structure, due to the movements of the magma, which developed a fluidal and, in the later stages of intrusion, a protoclastic structure in the rock; (4) The granite-gneiss of the bathyliths not only arched up the invaded strata into a series of domes, but 'stoped' out portions of the sides and lower surface of the arches, the fragments torn off from walls and roof by the invading granite being found scattered throughout the mass of the invading rock: this 'stoping,' however, probably developed only a small part of the space which the granite now occupies; (5) The invading granite not only exerted a mechanical action upon the invaded strata, but also gave rise to a variety of metamorphic products, among others amphibolite produced by its action in the limestone, which accounts for the fact that while the invaded strata are chiefly limestone, the fragments of the latter, where found in the granite, consist of amphibolite; (6) The invading bathyliths and allied intrusions of granite occupy the greater part of the great Northern Protaxis of Canada, which has an area of approximately 2,000,000 square miles. It has, therefore, been considered advisable to restrict the name Laurentian to this great development of the 'Fundamental Gneiss,' which, although intrusive into the Grenville Series, nevertheless underlies and supports it: (7) The relation of the Grenville Series, which forms the base of the sedimentary portion of the geological column in Eastern Canada, to the Huronian and Keewatin Series, which are the oldest stratified rocks in the western part of the Protaxis, has yet to be determined, the two not having so far been found in contact; nowhere, moreover, either east or west, has the original basement on which the first sediments were laid down been discovered; these are everywhere torn to pieces by the granite-intrusions of the Laurentian.

November 20th.—Sir Archibald Geikie, K.C.B., D.C.L., Sc.D., Sec. R.S., President, in the Chair.

The following communications were read:-

1. 'Glacial Beds of Cambrian Age in South Australia.' By the Rev. Walter Howchin, F.G.S., Lecturer in the University of Adelaide.

The known extension of the beds in question is 460 miles from north to south (Onkaparenga River to Willouran Range). The

greatest width across the strata between Port Augusta, at the head of Spencer's Gulf, in an easterly direction to the Barrier Ranges of New South Wales, is about 250 miles. The beds occur as part of a great conformable series, in the upper part of which Cambrian fossils have been found. The rocks above the Glacial Beds are mainly purple slates and limestones; below they are quartzites, clay-slates, and phyllites, passing into basal grits and conglomerates, resting on a pre-Cambrian complex. The beds consist of a groundmass of unstratified indurated mudstone, more or less gritty, carrying angular, subangular, and rounded boulders, up to 11 feet in diameter. In most sections there are more or less regularly-stratified bands. The thickness of the glacial series has been proved up to 1500 feet. The commonest rock-type among the boulders is a close-grained quartzite; but gneiss, porphyry, granite, schistose quartz, basic rocks, graphic granite, mica-schist. and siliceous limestone occur. The discovery of ice-scratched boulders has placed the origin of the beds, according to the author. beyond doubt. The strix are often as distinct and fresh-looking as those occurring in a Pleistocene boulder-clay. Up to the present, eighty definitely-glaciated boulders have been secured, besides the known occurrence of other erratics too large for removal. Under strong pressure and movement in their bed, some of the boulders exhibit evidences of abrasion; but this produces features which cannot well be confounded with those due to glaciation. pressure that has induced cleavage has caused the elongated boulders to revolve partly in their bed and place their long axes parallel to the cleavage-planes. In this movement, some of the stones have become slightly distorted, and many show the effect of fracture in the form of pseudo-striation on exposed surfaces. The lines, however, are of equal size and depth, and parallel to each other over wide surfaces; while the glacial striæ are generally patchy in their occurrence, of varying intensity, and divergent in direction. A series of illustrative sections are described. It is considered that Mr. H. P. Woodward's suggestion, that the 'boulder-clay' had its origin from 'floating ice,' appears to be most in accordance with facts. The interbedded slates and limestones may possibly indicate the occurrence of interglacial conditions.

2. 'On a Formation known as "Glacial Beds of Cambrian Age" in South Australia.' By H. Basedow and J. D. Iliffe.

Some 8 miles south of Adelaide a typical exposure of the conglomerate is bounded to the east by a series of alternating quartzitic and argillaceous bands of rock, comprising the central and western portions of a fan-fold, partly cut off by a fault. Further evidence of stress in this margin is given in the fissility, pseudo-ripple-marks, contortion and fracture, and obliteration of bedding in the quartzite-bands, and in the pinching-out of them into lenticles and false pebbles. On the west side the conglomerate is bounded by the 'Tapley's Hill Clay-Slates,' and there is evidence from the nature of the junction-beds that the conglomerate itself is isoclinally folded.

In that portion of the conglomerate which is adjacent to its confines, 'boulders' of quartzite are apparently disrupted portions of quartzite-bands, since these are in alignment with the truncated portions of bands still existing, and are of similar composition. The authors are not at present in a position to account for the presence in the conglomerate of boulders of rocks foreign to the beds that border the conglomerate, or of such as possess markings comparable to glacial striæ, by their theory of differential earthmovements; but they consider that a boulder-bed subjected to lateral pressure would probably lend itself to the production of 'false pebbles,' through the disruption of intercalated hard bands within itself or on its boundaries.

## XVI. Intelligence and Miscellaneous Articles.

A THEORY OF THE DISPLACEMENT OF SPECTRAL LINES PRODUCED BY PRESSURE.—A CORRECTION.

MY attention has been drawn by Professor W. J. Humphreys to a slip on page 576 of my paper under the above title in volume 14 of this Journal. Since the formula for  $\delta\lambda$  towards the bottom of the page is in electrostatic units, the datum  $e/mc = 1.8 \times 10^7$  should be replaced by  $e/m = 1.8 \times 10^7$ . The value of  $\delta\lambda/\lambda_0$  is  $8 \times 10^{-11}$  per atmosphere as stated.

O. W. RICHARDSON.

Princeton, N. J., Dec. 9, 1907.

#### LORD KELVIN.

WITH the beginning of a new volume we have to mourn the loss of Lord Kelvin. Ever since the year 1871, when Sir William Thomson's name first appeared as one of the Editors of the Philosophical Magazine, this journal has been very deeply indebted to him for his kindly interest and invaluable advice, as well as for many contributions of the highest value.

Notwithstanding the incessant calls on his time and energy, arising from his numerous public duties as well as from his unintermittent scientific labours, he was never too busy to give his ungrudging help to the Magazine whenever it was sought.

Our readers will doubtless join with us in an expression of profound admiration of Lord Kelvin's intellectual greatness and of affectionate regard for the simple kindliness of his nature.



Fig. 1.

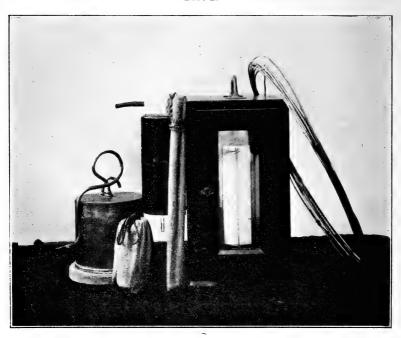
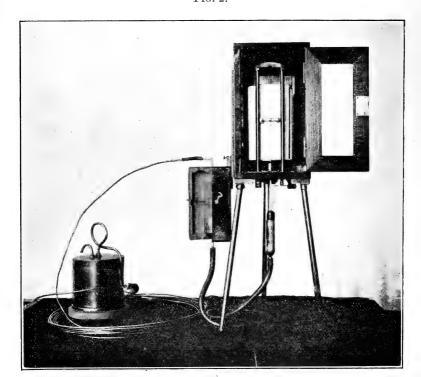
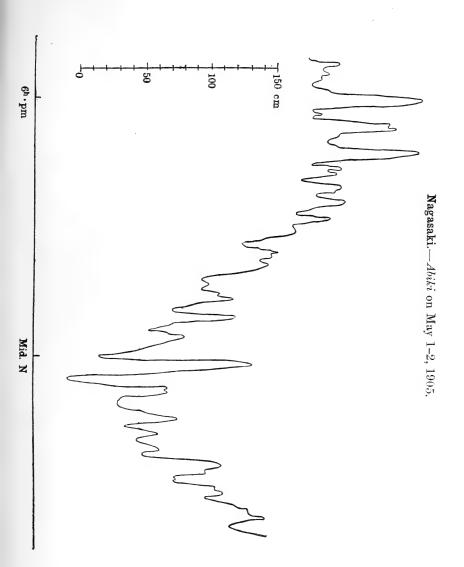


Fig. 2.









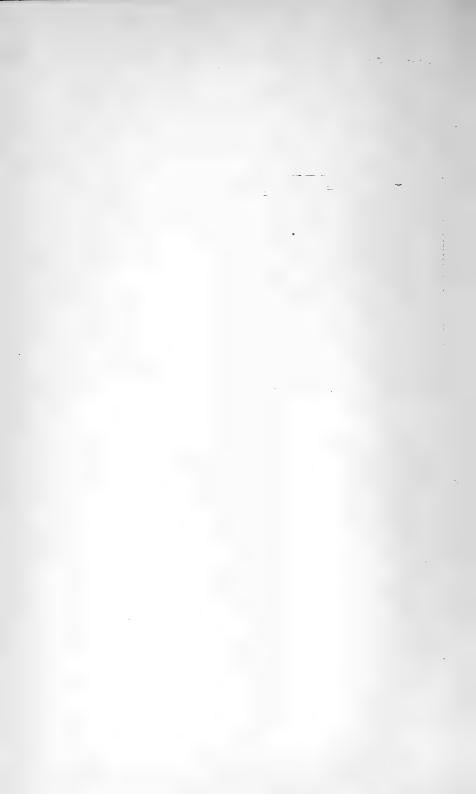


Fig. 1.

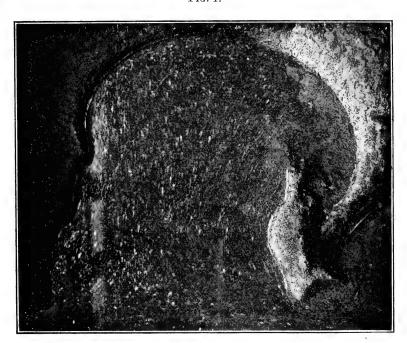
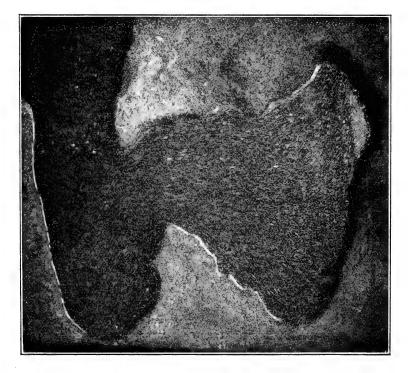


Fig. 2.







Frg. 1.



Fig. 2.



Phil. Mag. Ser. 6, Vol. 15, Pl. VI

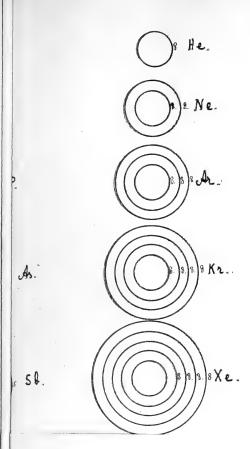


Fig. 2.





Phil. Mag. Ser. 6. Vol. 15. Pl. VII.

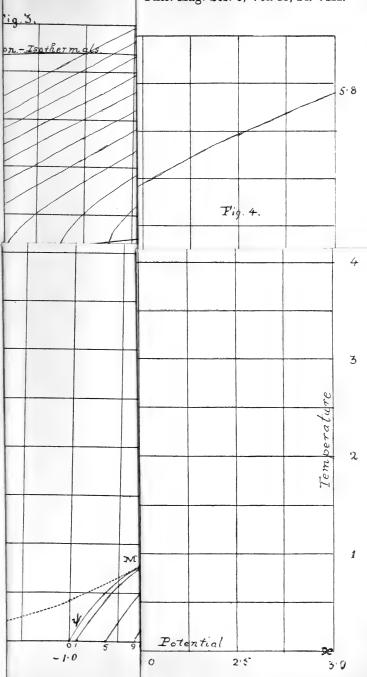




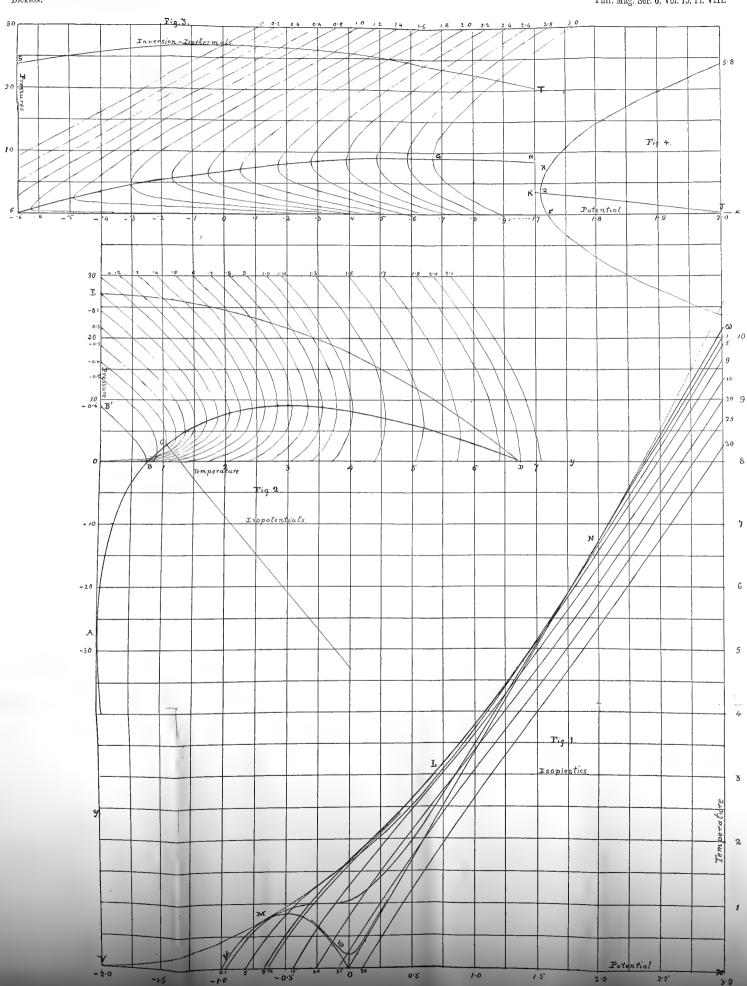
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Phil. Mag. Ser. 6, Vol. 15, Pl. VIII.











CAMPBELL'S VARIABLE MUTUAL INDUCTANCE.



INDE

#### THE

## LONDON, EDINBURGH, AND DUBLIN

# PHILOSOPHICAL MAGAZINE

AND

# JOURNAL OF SCIENCE.

[SIXTH SERIES.]

### FEBRUARY 1908.

XVII. On certain Phenomena exhibited by Small Particles on a Nernst Glower. By C. E. Mendenhall and L. R. Ingersoll \*.

In the course of some recent work on the determination of high temperature melting-points (see Phys. Review, July 1907), the present writers noted several rather curious phenomena attending the heating of minute particles of various metals placed upon the surface of a Nernst glower—whose temperature could be controlled with a suitable rheostat—and examined with a microscope of low power. These phenomena seemed sufficiently novel and interesting to merit separate study, and the results of our observations are contained in the present paper.

Phenomena of Undercooling of Molten Globules.

The first phenomena are associated with an undercooling of molten globules which is so great as to be in itself worth noting. If a small particle of, say, platinum be placed on the glower, melted into a globule about 1/10 mm. or 1/20 mm. in diameter, and then allowed to cool either slowly or rapidly, it will not solidify at the melting temperature, but will remain very evidently fluid until a temperature is reached from 50° to 300° lower than the melting-point, when solidification will suddenly occur, accompanied by a quick "flash" or brightening of the drop. Upon reheating there is no flash and the drop melts at its proper melting temperature. The same

general effect is observed with gold, palladium, platinum,

silicon, rhodium, and iridium.

The only record we can find of the previous observation of such an effect is that given in Winkelmann's Handbuch (II. 1, p. 487, 1st. ed.), where the flash is considered to be a luminescent phenomenon associated with the giving off of absorbed hydrogen by silver, no mention being made of undercooling. The article refers to a paper by Dr. T. L. Phipson (B. A. Report, 1859, p. 76), who noted such a flash in cooling a globule of silver, just at its melting-point.

It seemed to us worth while to determine more closely the conditions which made possible the retention of the fluid state at temperatures as much as say 300° below the normal melting-point—especially to see if the occlusion of gases played any great part in it, and also to see whether the brightening of the drop was a luminescent effect connected directly with molecular rearrangement—or simply a temperature effect due to the liberation of the latent heat of fusion. Microscopic examination of the particle shows conclusively that the flash accompanies a change of state, for in general there is a marked change from a smooth surface often showing decided motion, to a rough, corrugated, and very evidently solid surface.

Bearing upon the problem as stated above we have noted

the following:—

The temperature at which "flashing" occurs is extremely variable. In general the smaller the drop and the higher its melting-point, the more it can be undercooled before flashing occurs; the difference in this respect between a drop 1 mm. in diameter and one 2 mm. in diameter is quite noticeable. The more the globule works into and imbeds itself in the glower material, i.e. the more it departs from a spherical form, the less it can be undercooled. The possible undercooling is also slightly less if the cooling occurs rapidly. The melting must be thorough and complete or else no undercooling whatever will occur. Granted thorough melting, further heating above the melting-point seems to be without influence \*.

The behaviour is essentially the same if the glower is placed in an atmosphere of CO<sub>2</sub>. Flashing also occurs in the same way if the globule is heated on a non-conducting clay surface, *i.e.* a Nernst-glower heater. The phenomenon was readily obtained with gold particles on such a heater, and

<sup>\*</sup> Tapping the support of the glower did not affect the undercooling which, considering the minute particles involved, is only what might be expected.

also with silver if care was taken to protect the silver from direct contact with the clay surface. For in the latter case it would not form a globule but simply flux into and be absorbed by the clay surface, just as was the case when tried on the Nernst glower itself.

The brightness of the flash increases with the extent of undercooling. Flashing appears to precede the solidification; with a large drop the flash is noticeably more prolonged than with a small one, and very evidently occurs before the

solidification.

From these facts we conclude that the phenomenon is simply one of exaggerated undercooling made possible because we are dealing with a very small mass of metal which assumes an approximately spherical shape. Furthermore, that the flashing is not a direct luminescent phenomenon but is due to the sudden increase in temperature resulting from the liberation of the latent heat of fusion; the longer duration of the flash in the larger globules corresponding to the greater amount of heat which must be dissipated. Probably, then, the previous observations referred to are erroneously classified as "luminescent."

We have made a number of measurements of the temperature at which flashing occurs, but these seem without interest except to note the maximum degree of undercooling which has been observed, namely, about 370° C. for both rhodium and platinum. That is to say, rhodium, which melts at about 1910° C., has remained molten as low as 1540° C.; and platinum, melting at 1745° C., as low as 1370° C.

In the case of rhodium we have observed a second anomaly at about 1050° C., consisting of an easily reversible change in the radiating power of the surface of the drop. As the temperature is lowered the drop becomes at about 1050° C. rather suddenly brighter—the change being seen to spread rapidly over the globule—and remains so (relative to the glower). If the temperature is again raised the reverse change takes place. The effect may be due to a molecular rearrangement, or to the absorption of some gas, but in either case the energy changes involved must be small, otherwise flashing or some similar temporary recalescent change would be observable.

Phenomena of Motion of Particles.

Quite distinct from these cases of undercooling are a number of cases of motion of various metals on the surface of the glower parallel to the current flow. The most striking of these is observed when a small particle of cobalt, say, is placed on the surface of a glower carrying a direct current. When the temperature is raised to about 1200° C. it will commence a slow and regular end-over-end rolling motion along the glower, which changes in direction when the current is reversed, and which is not affected by holding the glower vertical, or, indeed, by turning it completely upside down. It is regretted that a somewhat careful study of this and the allied phenomena has not led as yet to as definite and satisfactory an explanation of the cause as might be desired; although of course it may be said at once that, as the glower is an electrolytic conductor, such motions are probably related to the other, and little understood, motions of matter in an electrolyte which have been observed many times (see discussion in Winkelmann) although the connexion is not very obvious. Our observations and such conclusions as we have been able to draw may not, however, be without interest, and will be discussed under two heads corresponding to two distinct, although evidently related, effects which have been observed, namely:—

(a) A rolling or sliding of molten globules of metal on the

surface of the glower.

(b) A motion of solid particles of metals and their oxides. This is the curious end-over-end rolling above-mentioned which will take place with particles of the most irregular

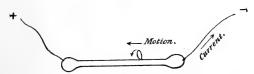
shape.

Case a.—A rolling or sliding of molten globules of metal has been observed with most of the metals which will melt into a globule on the glower; rhodium perhaps showing it the best. The motion may be slow and accompanied by a plowing up of the surface of the glower as if the globule were trying to embed itself, or—and this is especially true just when the substance is first melted—it may be as fast as the eve can follow. In direction \* it may be either with or against the current, according to the metal used, and in every case where both can be observed agrees as to direction with the motion in the solid state described below (Case b). With gold and platinum the motion is with the current. This rolling is very possibly similar, as to cause, to an effect noted, we believe by Quincke, in which a globule of mercury placed in a tube of acidulated water is observed to move rapidly, only in this case against the current.

\* This rolling has also been observed, in the same direction, with rhodium on special glowers composed of MgO and  ${\rm Al_2O_3}$ , instead of the oxides of ziroonium and yttrium as is the case with commercial glowers; so that it does not depend on the special constitution of the glower.

Case b.—Motions of solid particles of metals and their oxides. These effects are so striking that we have been led to collect considerable data concerning them. To describe in detail a typical case which has already been mentioned:—If a sliver of cobalt, say 2 mm. long and 2 mm. thick, is placed lengthwise on a glower carrying direct current, at a temperature below the cobalt melting-point, it will slowly rise on end and continue turning over till it again lies flat, the process being repeated so that the metal as a whole moves along the glower against the current flow; and the motion will continue till the particle stops on the cool glower terminal (see fig. 1). A more exaggerated case—and one which

Fig. 1.



shows that the forces, such as they are, must be comparatively large, if they are assumed to act only on the small area of the particle in actual contact with the glower—is that of a horseshoe-shaped piece of metal, say 4 mm. in diam., hung over the glower, with its plane at right angles to it. This will slowly turn (in the same sense as before) until its prongs point upward when it usually becomes unstable and falls off.

In an attempt to explain these actions we have noted the following facts:—

(1) The motion always reverses with reversal of current, and this is true no matter what the position of the particle, whether it is just rising from a horizontal position, or standing vertical. For some metals the motion is with, for others against, the direction of the current, as ordinarily defined. In Table I., column headed "direction," a + sign means motion with the current, a - sign motion against the current.

(2) The rapidity of the motion under similar conditions varies greatly in different metals. In the column headed "magnitude," the numbers are roughly proportional to the rapidity of the motion, cobalt and copper being by far the best in this respect. The actual velocity of progression along the glower of a small piece of either of these metals would in a favourable case be a matter of perhaps a centimetre per minute. With most metals, however, the motion is so slow that it is practically impossible to get a progressive end-overend translation of the particle along the glower; so in taking

the observations which form Table I. the effect was considered to exist when a particle showed a definite tendency to tip over one way or the other, the direction reversing with reversal of current.

(3) The size and shape of the particles is not important, most irregular shaped particles rolling as readily as nearly round ones; in general small particles have a more rapid angular motion, though they may not cover as much ground. Long flat pieces usually move very readily even when touching the glower only at the tip. The forces involved are not at all proportional to the size of the particle, but are sufficient to move small particles up a vertical glower against gravity. The fact that particles will also move along the under side of the glower, and that they are found to be more or less firmly stuck to the glower when it is allowed to cool, indicates that there is incipient fluxing or sticking of the metal to the glower even at temperatures below the melting-point.

(4) The rapidity of the motion increases both with the temperature of the glower and the current density in it. By superposing a direct on an alternating current through the glower (the latter doing most of the heating, and the former serving to direct the motion), we have into measure separated current and temperature influence, and, find that the current is the more important of the two. If the current density in the glower is sufficient, the motion will take place at a temperature a good deal below the melting-point of the metal: for example, cobalt, which melts at say 1500° C., has been observed to move at 1150° C. In general the higher the melting-point of the metal, the higher the temperature necessary to produce noticeable motion.

(5) We have attempted to influence the motion by producing electrostatic and electromagnetic fields near the particle on the glower, but without success. Nor could the motion be produced on a hot piece of glower material not carrying a current, but having electrostatic and magnetic fields along and at right angles to it in such a way as to simulate the effects of a current. Negative results were also obtained when particles supported on mica were brought up underneath a running glower to within microscopic distances

of its surface.

(6) We have not been able to produce the effect on any metallic conductor, nor have we succeeded in observing it on any electrolytic conductor which differed much in composition from the ordinary Nernst glower, the trouble being either that these became molten and sticky at too low a temperature and with too small a current density (for

example glass or common salt), or require too high a temperature (for example MgO). The phenomena were, however, readily produced on a glower made of pure zirconium oxide. No motion will occur over a thin layer of MgO coated on a glower surface,—probably because under these circumstances

the MgO carries practically no current.

(7) A particle of a given metal moves with difficulty if at all over a part of the glower which has been fluxed \* with the same metal. The motion of another metal over this part of the surface is in general not so much altered by this fluxing of the first. Heating for a short time at a high temperature will remove these effects produced by the fluxing in of any metal, probably because the metal is vaporized off in this process.

(8) Placing the glower in an atmosphere of CO<sub>2</sub> or in a one-millimetre vacuum does not perceptibly alter the effect. Nor does a jet of oxygen blown at the glower or particle make any difference, unless it be strong enough to cool the particle considerably, especially at its point of contact with the

glower.

(9) Oxides of many metals (see Table, p. 212) show a

similar motion;

- (10) In the table the approximate atomic weights of zirconium and yttrium (whose oxides are the principal constituents of the glower) are inserted, and it will be noted that, with two exceptions (boron and ruthenium), all metals having an atomic weight greater than these metals move with the current, and those with lower atomic weights move against the current. In order to test further this rather striking, but probably accidental arrangement, we have made many attempts to observe the motion on glowers made of oxides of metals having much smaller atomic weights—especially MgO and Al<sub>2</sub>O<sub>3</sub>—in order to see whether the motion of cobalt, for example, would be reversed on such a glower. So far we have been entirely unsuccessful in observing anything but the motion of molten globules (above referred to) on such a glower, and the metals which make molten globules have almost all higher atomic weights than the zirconium of the ordinary glower, so no reversal would be expected in this case. But this negative result is by no means conclusive, for, in the first place, it is extremely difficult to make a glower of Mg and Al oxides which will run on direct current
- \* With most metals (the less oxidizable metals such as gold, platinum, rhodium, and iridium are exceptions) heating to a sufficiently high temperature results in the metal soaking into and fluxing with the glower material.

TABLE I.

TABLE 1.												
	Atomic Weight.	Dirrction of motion when molten.	Motion when solid.				of ten.	Motion when solid.				
Substance.			Direction	Magnitude	Substance,	Atomic Weight.	Direction of motion when molten.	Direction	Magnitude			
Boron	10.9		+	3	Rhodium	103	+	+	1/2			
Magnesium	24				Palladium	106	•••	+	2			
Oxide	•••	•••	_	2	Silver	108		+(?)				
Silicon	28	-	-	1	Barium	137						
Titanium	48			5	Oxide	•••	• • • • • • • • • • • • • • • • • • • •	+	1			
Chromium	52		_	1	Tantalum	183						
Manganese .	55	***	_	1	Oxide	•••		+	1			
Iron	56				Iridium	193		+	1			
Oxide		***	_	5	Platinum	195	•••	+	i			
Cobalt	58.7		-	10	Gold	197	+	+(?)				
Nickel	58.6			1								
Copper	63.2		-	10								
Yttrium	89	Materials of Glower.										
*Zirconium	90 105											
Ruthenium.	102		-	2								

<sup>\*</sup> Zirconium not being properly speaking, an element, the atomic weight of the particular "fraction" contained in the glower is uncertain to about the extent indicated in the table.

for more than a minute or two, and then only very unsteadily, especially at low temperatures; and, secondly, the resistance of these oxides is so high that the current corresponding to a given temperature is very much less than with the ordinary glower. The circumstances of observation, then, are much less favorable, and the effect to be expected much less in amount than with ordinary glowers.

Besides these cases of mass motion we have noted two cases of real or apparent diffusion of metal along the glower. The first occurs when a particle of metal (gold, platinum, and the less oxidizable metals excepted) is heated until it melts and fluxes with the glower. In some cases this means

simply a sinking of the metal into the material of the glower without apparent motion in either direction, but with some metals the process involves vigorous action, and shows a very definite tendency to proceed in one direction, depending on the current (see Table I.). Fluxing may be carried to a point where the conduction in the glower becomes largely metallic instead of electrolytic, and that part of the glower in consequence becomes relatively cool. Continued heating at a high temperature will vaporize most of such metals out of the

 ${f glower.}$ 

The second case, which is possibly one of only apparent diffusion, has been observed with platinum, rhodium, and palladium, and is probably characteristic of the less oxidizable metals. It consists in the formation of a discoloured streak or "tail" extending out from the drop along the surface of the glower and ending in a point. In the cases noted it has been directed against the current flow, when direct current was used (i. e. opposite to the direction of mass motion), while with alternating current it is found on both sides of the globule. In the case of platinum, it will occur at temperatures a hundred degrees or more below the melting-point, although the formation is more rapid at higher temperatures. scopic examination of such a platinum trace shows the surface of the glower covered with what is apparently a very thin layer of platinum for perhaps a millimetre from the globule. Nevertheless, chemical tests kindly made by Professor Lenher have so far failed to prove positively that the "tail" is metallic platinum; but the minute amount of material present makes chemical examination extremely difficult.

Undoubtedly these cases of diffusion, inasmuch as they are unidirectional and depend on the current, imply the existence of forces related to those which must cause the mass motions above described, but it is impossible to say at present just what this relation is; for there seems to be no fixed relation between the directions of diffusion and of mass motion in the

various cases.

#### Conclusion.

It seems probable that the motions of both solid and molten particles are due to the same causes; furthermore, that the forces involved, such as they are, are localized at the point of contact of the particle and glower. If we consider this fact in connexion with that before noted of the sticking of the particle to the glower, involving as it does considerable forces of cohesion between the metal and the glower, we may perhaps suggest a general explanation of the phenomena.

For some of the glower current may be supposed to pass around through the particle, and there would then be, on account of the electrolytic character of the glower conduction, oxygen given off where the current enters, and absorbed where it leaves, the metal, and thus the forces of cohesion on the two sides be rendered unequal. The result would be a couple tending to turn the particle or globule over in one direction. Somewhat similar conditions would exist in the case of a particle of oxide placed on the glower, as all oxides conduct more or less at these temperatures. It is not evident what determines the direction in which a particle will move, nor is there any apparent reason for the curious grouping with respect to atomic weights, of the metals moving with, and moving against the current, which grouping may indeed have little or nothing to do with the fundamental cause of the motion. A possible explanation of this grouping, however, might be based on the fact that the metals of higher atomic weights which can be tested in this way, are the less readily oxidizable ones which will form globules when molten, while those of lower atomic weights are more readily oxidized and flux with the glower when melted. That different metals should, under similar conditions, move oppositely is, from the view just given, not surprising. There are, however, several exceptions (for example, tantalum and barium, which are readily oxidizable) which are against this latter way of looking at the matter.

Physical Laboratory, University of Wisconsin, June 1907.

XVIII. Effect of Combined Stresses on the Elastic Properties of Steel. By E. L. Hancock, Assistant Professor of Applied Mechanics, Purdue University, La Fayette, Ind.\*

[Plates X. & XI.]

DURING the past year tests have been continued under the direction of the writer to determine the effect of combined stresses on the elastic properties of steel. These tests form a part of the general plan for such tests carried on in the laboratory for testing materials of Purdue University (see Proceedings Amer. Soc. Testing Materials, vol. v. p. 179, and vol. vi. p. 295). The tests already made and reported to this Society have included tests in tension and compression while the material was under torsion. The tests reported in this paper were made by first subjecting the material to tension or compression, and then while under such stress applying certain increments of torsion. In the tension-torsion

\* Communicated by the Author, having been read at the meeting of the American Society for Testing Materials on June 20, 1907. tests tensile stresses of 0, 33, 50, 69, 81, and 100 per cent. of the normal elastic limit in tension were first applied, and while the material was under such tension it was tested in torsion. In the compression-torsion tests compressive stresses of 0, 33, 50, 83, and 100 per cent. of the normal elastic limit in compression were applied, and while the material was under such stress it was tested in torsion. A third series of tests were made on full-sized steel shafting, by first subjecting the material to a certain torque, and then, while under such torque, testing it in flexure.

The writer hopes, at an early date, to be able to make a general review of all tests made, and to accompany it with a proper analysis of all data thus far obtained. In the mean-

time the tests themselves are reported.

Materials.—The material used in the tension-torsion and the compression-torsion tests was a grade of steel tubing furnished by the Shelby Steel Tube Co. The tension-torsion test-pieces were 32 inches long, one inch outside diameter, and 28/32 inch inside diameter. The compression-torsion test-pieces were 8 inches long and of the same size and thickness as the tension-torsion test-pieces. Simple tension tests showed the material to have the following physical properties:-Maximum strength 41,000 lbs. per sq. inch; elastic limit 21,000 lbs. per sq. inch and per cent. of elongation in eight inches of 32. It was thoroughly annealed and of uniform thickness. The material used in the torsionflexure tests consisted of solid nickel and mild carbon-steel shafting furnished by the Carnegie Steel Co. The nickelsteel was of the same chemical composition as the carbonsteel, except that it had about 3 per cent. of nickel. pieces of shafting tested were 5 feet long and turned down to 1.5 inches in diameter. These pieces were squared slightly at the ends to provide for the application of the torque.

Method of Test.—The method of testing pieces in tension while already under torsion has been explained (see Proc. Amer. Soc. Test. Mat. vol. v. p. 179). The same apparatus and arrangement of apparatus was made use of in testing in torsion while under tension. After the desired tensional load was applied, sufficient torsional load was put on to overcome the friction of the ball-bearing heads, and then the piece was tested in torsion. Elongations were measured with a Johnson extensometer and torsional deformations by means of an Olsen troptometer. Deformations in both tension and torsion were measured on an eight-inch gauge length. To determine the torque necessary to overcome the friction of the ball-bearing heads, due to the tensional load, the troptometer was set at zero, and sufficient sand added to the pails at the ends

of the arms to cause a perceptible motion. This method

proved accurate and satisfactory.

In making the compression-torsion tests, the upper ballbearing head was placed upon the platform of the testingmachine with the same side up as when it was on top of the machine. The other ball-bearing head was left on the under side of the moving head of the testing-machine. In this position the compression specimen was inserted, and the same set of jaws that applied tension and torsion in the tests just described, applied compression when the moving head of the machine was lowered, and afterward applied torsion. compression specimens were 8 inches long, and this length, after allowing 2.5 inches on each end for insertion in the jaws, gave a compression length of 3 inches. Compression and torsion were both measured on a two-inch gauge length. Deformations were measured with an Olsen compressometer and troptometer. The disposition of the specimen in the machine and the arrangement of the compressometer are shown in Plate X., although this is not a photograph of one of the test-pieces and the troptometer is not shown. Torsion loads were obtained by adding the required amount of sand to the pails attached to the ends of the arms, in a manner similar to that used in the tension-torsion tests. After the required compressional load was applied, sufficient sand was placed in the pails to overcome the friction of the ball-bearing heads.

This was indicated by a perceptible movement of the troptometer index. In making these compression-torsion tests great care was used to avoid any possible column action of the specimen. It is believed by the writer that no such action took place in the case of any tests reported in this paper.

The torsion-flexure tests of nickel- and carbon-steel shafting were made by means of specially devised apparatus. The same arms used in the preceding tests were attached to the ends of the specimen. The attachment of these arms and the general disposition of the specimen with relation to the testing machine is shown schematically in Pl. XI. fig. 1. The testingmachine, upon which the apparatus was mounted, and which was used in the flexure part of test, was an ordinary tension machine of 20,000 lbs. capacity. The torque was applied by means of weights, indicated in the drawing by the arrows P<sub>1</sub>. The plan throughout was, first, the application of a certain torque, and then while the shaft was under this torque subjecting it to a flexure test. While the torque was being applied the knife-edge A was removed, allowing the shaft to turn freely over the knife-edge B. When the desired torque had been applied, the knife-edge B was removed and the

knife-edge A inserted. The downward force P<sub>1</sub> at the end of the shaft indicated by A was obtained by allowing the desired weight to hang from the end of the arm. The upward force P<sub>1</sub>, at the same end A, was obtained by allowing the desired weight to hang from a bicycle chain which ran over a suitably mounted bicycle wheel and fastened to the other end of the arm, in such a way as to give the required vertical upward pull. The friction of the wheel and chain were negligible. The arm at the end C was the fixed arm. The specimens were tested in flexure by applying the loads P at the centre by means of the testing-machine. Torsional deformations were measured on a gauge-length of 4 feet 9 inches by means of an Olsen troptometer. Flexural deformations were measured with an Olsen deflectometer. After the torque had been applied the beam of the testing-machine was balanced, eliminating from consideration the weight of the cross-beam and the weights used in applying the torsion.

Results.—The lowering of the torsional elastic limit of steel tubing due to the various tensional loads is shown by Pl. XI. fig. 2. Curve 1 shows the results of simple torsion tests, Curve 2 the results of torsion tests while the material was under tension to 2/6 the elastic limit in tension. Curves 3, 4, 5, and 6 show the results of torsion tests while the material was under tension of 3/6, 4/6, 5/6, and 6/6 respectively the elastic limit in tension. Each curve represents, at least, an average of The results of the compression-torsion tests two tests. are shown by fig. 3. Curve 1 shows the results of simple torsion tests of the material. Curve 2 shows the results of torsion tests while the material was under a compression of 2/6 the elastic limit in compression. Curves 3, 4, and 5 show the results of torsion tests while the material was under compression to 3/6, 5/6, and 6/6 respectively the elastic limit in compression. Each curve represents an average of two or more tests. The values of 2/6, 3/6, &c. of the elastic limit were not in every case exactly noted, but the results used in the tables and curves show a discrepancy in only one or two cases.

The results of the torsion-flexure tests of nickel- and carbonsteel are shown by figs. 4 & 5 (Pl. XI.). Fig. 4 shows the results of the tests of mild carbon-steel shafting. Curve 1 shows the result of a flexure test of a piece of the shafting when no torsion is applied. Curve 2 shows the results of a flexure test of a similar piece of shafting while it was under a fibre stress of 22,800 lbs. per sq. inch on the outer fibre. Curves 3 and 4 show the results of flexure tests of shafting while under a stress on the outer fibre, due to torsion, of 30,400 and 38,000 lbs. per sq. inch respectively. Fig. 5 shows the results of tests of nickel-steel shafting. These pieces of shafting were the same size as those of carbonsteel. Curve 1 shows the result of a simple flexure test. Curves 2, 3, 4, and 5 show the results of flexure tests while the material was under a torque sufficient to produce a fibre stress in the outer fibre of 15,200, 22,800, 30,400, and

38,000 lbs. per sq. inch, respectively.

The change in the elastic limit in tension, torsion, and flexure due to the presence of another stress—torsion, tension, compression, and torsion—is shown in fig. 6. The abscissæ represent the amount of the particular stress initially applied, and the ordinates the portion of the elastic limit (normal elastic limit) obtained in tension, torsion, and flexure as a result of the initial stress. All the results that have been obtained by the writer are shown in the diagram, so that, not only are the tests made during the past year represented, but also all those that have been reported heretofore. These points are averaged by lines 1, 2, 3, and 4 in fig. 7. The figure needs no explanation.

The change in the unit stress at the elastic limit, part of deformation at elastic limit, and the modulus of elasticity are shown by fig. 8. The amount of stress applied initially is represented on the horizontal axis, and the corresponding change produced by this initial stress is shown on the vertical axis. It is seen that the unit stress at the elastic limit, deformation, and modulus of elasticity are all lowered by the

stress initially applied.

The results obtained from the tests of steel tubing, in torsion while under tension, are shown in Table I. The table shows that an amount of tension applied, equal to 0, 33, 50, 69, 81, and 100 per cent. of the elastic limit in tension, produces an elastic limit in torsion of 100, 68, 60, 43, 31, and 25 per cent. of the normal elastic limit in torsion respectively. The same table also gives the results of the compressiontorsion tests, showing that an amount of compression applied, equal to 0, 33, 50, 83, and 100 per cent. of the normal elastic limit in compression, produces an elastic limit in torsion of 100, 73, 42, 36, and 27 per cent. of the normal elastic limit in torsion respectively. It is seen from this table, as well as from fig. 8, that the unit stress and unit strain at the elastic limit are lowered considerably due to the combined stresses, and that the modulus of elasticity is also lowered, but to less degree. That is, the strength of the material suffers most when combined stresses are acting.

The results of the flexure tests on steel shafting are shown in Table II. Here the nickel-steel seems to withstand the combined stresses better than the mild carbon-steel. This is seen by comparing the percentage of normal elastic limit, for the carbon-steel 100, 87, and 67, and for the nickel-steel 100, 90, 83, 77, and 70. The percentage of normal deflexion at the centre for carbon-steel is seen to be 100, 92, and 79, while for nickel-steel it is 100, 98, 100, 99, and 89. The modulus of elasticity is changed but little in either case, that is, the combined stresses have little effect upon the stiffness of the

shafting.

Table III. gives the bending moments in both torsion and flexure for both carbon- and nickel-steel shafting. Table IV. gives the results of computing unit stresses by the various formulæ for combined stresses. The first and second columns give the greatest tension and shear respectively, on any internal plane, when no account is taken of the change of form due to the acting stresses. The third and fourth columns give the greatest tension and shear respectively, on any internal plane, when it is assumed that Poisson's ratio is 1/4. sixth columns give the greatest tension and shear respectively, on any internal plane, when it is assumed that Poisson's ratio The last two columns give the unit tension and unit shear on the outer fibre applied to the specimen during the In the case of the compression-torsion tests the first, third, fifth, and seventh columns give unit compression instead of unit tension. (For the formulæ from which these results have been computed, reference is made to a former communication of the author, see Proceedings of Amer. Soc. for Test. Mat. vol. vi. p. 295; Phil. Mag. vol. xii. p. 418, 1906.)

#### Conclusions.

The results of tests reported in this paper show:—

(1) That combined tension and torsion lowers the elastic

limit in torsion, as shown in fig. 7.

(2) That combined compression and torsion lowers the elastic limit in torsion in about the same way as in the case of tension-torsion.

(3) That combined torsion and flexure lowers the elastic limit of the materials in flexure, as shown in figs. 6 and 7, and that this lowering seems to be less than for any other case of combined stresses thus far investigated. This lowering is slightly less for the nickel-steel shafting than for the carbon-steel shafting.

(4) That the unit deformation at the elastic limit of the tubing in tension-torsion and compression-torsion is lowered,

as shown in fig. 8.

(5) That the deflexion of the steel shafting is made less when the torsion is increased, the change being greater in the case of the carbon-steel than in the case of the nickel-steel. (Deflexion here means deflexion at the elastic limit.) A

comparison of figs. 4 and 5 shows that, within the limits of elasticity, the amount of deflexion for any given load is about the same for the carbon-steel as for the nickel-steel.

(6) That the modulus of elasticity, both in torsion and flexure, is lowered slightly by the presence of combined

stresses (fig. 8).

(7) That the maximum shear on any internal plane should control in design of parts subjected to combined stresses. In Table IV. the computed maximum tension and maximum shear that is greater than the tensile or shearing strength of the material has been underlined. It is seen that in only a few cases does the maximum tension exceed the tensile strength of the material, while the computed maximum shear is, in very many cases, greater than the shearing strength of the material. These results are generally in accord with results previously obtained by the writer.

Table I.

Results of Tests of Steel Tubing, Tension-Torsion, and Compression-Torsion.

Tension stress, lbs. per sq. inch. applied.	Per cent. of elastic limit in tension.		Per cent. of elastic limit in torsion.			Modulus of elasticity of shear, lbs. per sq. in.	Per cent. of normal modulus of elasticity.
0	0	10500	100	·0021	100	10350000	100
7000	33	7200	68	.0017	82	9075000	87
10500	50	6300	60	.0013	64	10350000	100
14000	89-	4500	43	·0011	53	9075000	87
17000	81	3300	31	.0007	35	9680000	93
21000	100	2700	25	0007	35	8086000	77

### Compression-Torsion Tests.

Note.—For these results the word tension in the first two columns above should be changed to compression, otherwise the headings are the same.

8000	0	10500	100	.0021	100	10000000	100
8000	33	7700	73	0022	104	7000000	70
12000	50	4500	42	.0012	57	7500000	75
20000	83	3800	36	·0018	85	4200000	42
24000	100	2900	· 27	.0012	57	5000000	50
		'	1	1	1		

TABLE II.

Results of Tests on Mild Carbon- and Nickel-Steel Shaftings in Flexure while under Torsion.

			MIL	D CARBON	-STEEL.			
Speci- men.	Shear applied, lbs. per sq. in.	Elastic limit in flexure, lbs. per sq. in.	Per cent. of normal elastic limit.	Modulus of elasticity in flexure, lbs. per sq. in.	Per cent. of normal modulus of elas- ticity.	Deflexion at elastic limit, in inches.	Per cent. of normal deflexion.	Per cent. of tor- sional elastic limit applied.
1	0	47000	100	32900000	100	•530	100	0
2	22800	41000	87	28400000	86	·490	92	75
3	30400	31000	67	32400000	- 88	·420	79	100
4	38000	22500	48	31500000	95	•280	53	125
NICKEL-STEEL.								
1	0	78500	100	33300000	100	·8 <b>40</b>	100	0
2	15200	68000	90	27700000	83	·820	98	40
3	22800	84000	83	31500000	94	·8 <b>40</b>	100	60
4	30400	59000	77	32300000	97	·830	99	80
5	38000	34000	70	32300000	97	.750	89	100

#### TABLE III.

Relation between the Bending Moment in Torsion and the Bending Moment in Flexure in the Torsion-Flexure Tests of Steel Shafting.

CA	RBON-STEE	NICKEL-STEEL.		
Specimen.	Torsional moment applied, in inch lbs.	Bending moment in flexure, in inch lbs.	Torsional moment applied, in inch lbs.	Bending moment in flexure, in inch lbs.
1	0	15150	0	24170
2	14400	12950	9800	21800
3	19200	9800	14400	20300
4	24000	7100	18200	18650
5	*****	•••••	24000	17000

Milia of Buress.	Apparen	Apparent Stresses.	I	$I = -\frac{1}{4}$ .	Tine	True Stresses. $I = \frac{1}{3}$ .	Simple	Simple Stresses.
	q1.	qe.	T <sub>1</sub> .	T.s.	$\mathbf{I}_1$ .	Lŝ	. b.	Ps.
Steel Tubing in Tension-Torsion.								
Simple Tension	21000	10500	21000	13100	21000	14000	21000	00000
Simple Torsion	10500	10500	13100	13100	14000	14000	00000	10500
1/3 TensE.L. Torsion	11500	8000	12600	10000	13000	10600	2000	7200
1/2 TensE.L. Torsion	13400	8200	14100	10200	14400	10900	10500	. 6300
·69 TensE.L. Torsion	15300	8300	15800	10300	15400	11000	14000	4500
-81 TensE.L. Torsion	17800	8100	17700	11300	17800	12100	17000	3300
1000 TensE.L. Torsion	21300	10800	21300	13500	21400	14400	81000	2700
Steel Tubing in Compression-Torsion	n.							
Simple Compression	24000	12000	24000	15000	24000	16000	24000	00000
Simple Torsion	10500	10500	13100	13100	14000	14000	00000	10500
1/3 CompE.L. Torsion	12600	8600	13800	10800	14200	11500	8000	2200
1/2 CompE.L. Torsion	13500	7500	13800	9300	14000	10000	12000	4500
.83 CompE.L. Torsion	20700	10700	20800	13300	20900	14200	20000	3800
*00 CompE.L. Torsion	24300	12300	24400	15400	24450	18400	24000	2900
Steel Shafting in Torsion-Flexure.		_	_		-			-
Mild Oarbon-Steel.				_				
Simple Flexure	41000	23500	47000	29300	41000	31300	47000	00000
3/4 Torsion-E.L. Flexure	51150	30880	23700	38300	24500	40800	41000	22800
4/4 Torsion-E.L. Flexure	48800	34100	54200	42800	22200	45400	31000	30400
5/4 Torsion-E.L. Flexure	21200	28800	83300	74800	87400	2000	22500	38000
Nickel-Steel.		_	-	_		-	. '	
Simple Flexure	76500	38200	78500	47800	78500	21000	76500	00000
Z/5 Torsion-E.L. Flexure	0027	37700	73000	47100	13200	00700	89000	15200
3/5 Torsion-E.L. Flexure	00217	28200	73060	49060	76100	52300	64000	22800
4/5 TOTSION-E.L. FIGEUR	72600	00074	70500	20000	80100	00400	00000	00400
n. Flexure	0000	00001	10000	00%00	0100	02100	0.3000	00000

XIX. The Groups of Isomorphisms of the Groups whose Degree is less than Eight. By G. A. MILLER \*.

THE main objects of the present paper are to develop some fundamental theorems relating to the group of isomorphisms of a known group, especially when it is represented as a substitution group, and to give a complete list of the groups of isomorphisms of all the abstract groups which may be represented on seven or a smaller number of letters. As the groups of low degrees present themselves most frequently, it is believed that such a list, if it is entirely reliable, will render good service. Fifty-four different abstract groups can be represented on seven or a smaller number of letters, while the number of distinct substitution groups on these letters is 95. A complete list of these groups is found in the 'American Journal of Mathematics,' vol. xxi. (1899) p. 326. In this list the distinct abstract groups are

denoted by Greek letters.

In accord with common usage the group of isomorphisms will be denoted by I, while the group under consideration and its holomorph will generally be represented by G and K respectively. The following known theorems are frequently used:—If a group is generated by two characteristic subgroups which have only the identity in common, its I is the direct product of the I's of these two characteristic subgroups, and its K is the direct product of their K's †. In particular, the K of an abelian group of order  $p_1^{a_1}, p_2^{a_2}, p_3^{a_3}, \dots (p_1, p_2, p_3, \dots$ being different prime numbers) is the direct product of the K's of the subgroups of orders  $p_1^{a_1}$ ,  $p_2^{a_2}$ ,  $p_3^{a_3}$ , . . . . symmetric group of degree n,  $n \neq 2$  or 6, is simply isomorphic with its, I, and the alternating group of degree n, n≠3, has the same group of isomorphisms as the symmetric group of the same degree. When n=2 the I is identity, and when n=6it is a well known imprimitive group of degree 12 and order 1440 ‡. It should also be remembered that the I of the cyclic group of order  $p^{\alpha}$ , p being an odd prime, is the cyclic group of order  $p^{\alpha-1}$  (p-1), and that the I of the cyclic group of order  $2^{\alpha}$ ,  $\alpha > 1$ , is the direct product of the group of order 2 and the cyclic group of order  $2^{a-2}$ .

<sup>\*</sup> Communicated by the Author.

<sup>†</sup> Transactions of the American Mathematical Society, vol. i. (1900) p. 396.

<sup>†</sup> Bulletin of the American Mathematical Society, vol. i. (1895) p. 258; Hölder, Mathematische Annalen, vol. xlvi. (1895) p. 345.

The theory of the groups of isomorphisms of cyclic groups includes the theory of primitive roots in number theory in view of the known theorem that the necessary and sufficient condition that a number (m) has primitive roots is that the I of the cyclic group of order m is cyclic. It has also been observed that some of the most useful theorems of number theory, such as Fermat's and Wilson's, are included in elementary theorems relating to the group of isomorphisms \*. Moreover, the groups of isomorphisms furnish one of the best means to construct groups having known subgroups, and in many other group-theory considerations they play a fundamental role which is continually receiving more attention.

### § 1. General Theorems.

THEOREM I.—If an abelian group G which involves operators whose orders exceed 2 is extended by means of an operator of order 2 which transforms each operator of G into its inverse, then the group of isomorphisms of this extended group is the

holomorph of G.

As the non-invariant operators of order 2 in the extended group correspond to themselves in every holomorphism of this group, its I may be represented as a transitive substitution group of degree n, where n is the order of G. After any holomorphism of G has been established, these operators of order 2 may be arranged in n different ways. Hence the order of I is n times the order of the I of G. Moreover, I contains an invariant subgroup which is simply isomorphic with G since we may obtain a holomorphism of the extended group by multiplying each operator of G by the identity and the remaining operators of the extended group by an arbitrary operator of G. It may be observed that this theorem includes the known theorem that the I of the dihedral group of order 2m, m > 2, is the holomorph of the cyclic group of order m.

THEOREM II.—The square † of a complete group which is not a direct product has the double holomorph of this group for its group of isomorphisms.

Let H and H' be two identical complete groups which are not direct products, and let G be the direct product of H

† The direct product of two identical groups is called the square of

one of them.

<sup>\*</sup> Cf. Transactions of the American Mathematical Society, vol. iv. 1903) p. 158; 'Annals of Mathematics,' vol. iv. (1903) p. 188.

and H'. We proceed to prove that H and H' are characteristic subgroups of G. Suppose that H" were another invariant subgroup of G which could correspond to H in a holomorphism. Hence H'' could be constructed by establishing some isomorphism between H and H' or between invariant subgroups. This isomorphism could not be  $(\alpha, 1)$ , since H does not contain any invariant operator besides the identity. If it were  $(\alpha, \beta)$ ,  $\alpha, \beta > 1$ , the quotient group with respect to the subgroup of order  $\alpha\beta$  would be composed of invariant operators under G. Hence H" could not be a complete group, as its constituents would admit outer isomorphisms under H and H' separately, since these groups do not contain any complete group invariantly. From this it follows that H must correspond either to itself or to H' in every holomorphism of G. As the holomorph of H is the square of H, it follows that this holomorph contains all the operators of the I of G which transform H into itself. Hence this I is the double holomorph \* of G. The preceding proof clearly also establishes the theorem: The direct product of two distinct complete groups neither of which is a direct product is a complete group.

THEOREM III.—The group of isomorphisms of the group obtained by extending a cyclic group of order 2m, m>2, by means of an operator of order 4 which transforms each operator of the cyclic group into its inverse is the holomorph of the cyclic group.

The proof of this theorem is similar to that of Theorem I.

THEOREM IV.—If a complete group has only one subgroup of index 2, the direct product formed with it and the group of order 2 is simply isomorphic with its group of isomorphisms.

Corollary I. The direct product of the symmetric group of order n,  $n \neq 6$ , and the group of order 2 is simply isomorphic with its I.

Corollary II. The direct product of the metacyclic group of order p (p-1), p being any odd prime, and the group of

order 2 is simply isomorphic with its I.

The proof of this theorem follows from the fact that such a direct product contains as a characteristic subgroup the subgroup of index 2 under the complete group, for if a group contains only one subgroup of half its order this subgroup is generated by its operators which are squares; and, vice versa, if a subgroup of index 2 is generated by operators which are squares, it is the only subgroup of this index. This

<sup>\*</sup> Transactions of the American Mathematical Society, vol. iv. (1903) p. 154.

subgroup corresponds to itself in every holomorphism of G. The invariant operator of order 2 also corresponds to itself. Hence G contains a characteristic subgroup of index 2, and each of the remaining operators may correspond to either of two operators after any holomorphism of this characteristic subgroup has been established. As the order of I is equal to that of G and as I contains a complete group which is simply isomorphic with the complete subgroup of index 2 in G, it follows that I is simply isomorphic with G.

THEOREM V.—The necessary and sufficient condition that an operator s of G transforms the operators of G according to an invariant operator under its group of cogredient isomorphisms is that the conjugates of s under G may be obtained by multiplying s by invariant operators under G. The highest order of such an invariant operator is the order of the corresponding

operator in the group of cogredient isomorphisms.

This theorem follows directly from the isomorphism between G and its group of cogredient isomorphisms. It is clear that a holomorphism corresponds to an invariant operator in the group of cogredient isomorphisms whenever the operators which correspond to themselves in the holomorphism constitute an invariant subgroup, the corresponding divisions are invariant, and the remaining operators correspond to themselves multiplied by invariant operators. Similarly, it may be observed that a holomorphism corresponds to an invariant operator of I when the operators which correspond to themselves in this holomorphism constitute a characteristic subgroup, the corresponding divisions are characteristic, and the operators of G which are not in the given characteristic subgroup correspond to themselves multiplied by characteristic operators of G.

Theorem VI.—If a substitution-group of degree n contains a subgroup of degree n-1 and involves no subgroup which is both of degree n and also of index n, then its group of isomorphisms is simply isomorphic with a substitution-group of

degree n which contains the given group invariantly.

No two substitutions of G could transform the n subgroups of degree n-1 in the same manner, since each substitution transforms these subgroups in the same manner as it transforms its elements \*. If an operator of I were commutative with each one of these n subgroups it would also be commutative with every operator of G. As this is impossible,

<sup>\*</sup> Bulletin of the American Mathematical Society, vol. ii. (1896) p. 145.

it follows that I is simply isomorphic with a substitution group of degree n and that the group of cogredient isomorphisms is simply isomorphic with G. This proves the theorem

in question.

If a substitution group G of degree n contains a subgroup of the same degree which leads to a representation which is conjugate to G, then G admits outer isomorphisms. particular, if a simple group appears only once among the total number of substitution groups of degree n, and if it involves a subgroup which is both of degree and of index n, then it admits outer isomorphisms. For instance, the simple group of order 168 presents itself only once among the substitution groups of degree 7 and contains a subgroup of degree 7 and order 24. It must therefore admit outer isomorphisms, as is also known from other considerations. it contains only one set of 7 subgroup of order 24 and degree 7, and as it is not invariant under a larger group of degree 7, its I can be represented as an imprimitive group of degree 14 which involves two systems of imprimitivity and is of order 336. Such considerations apply to a large number of substitution groups and are frequently useful to obtain I.

The group of isomorphisms of every finite group is finite. In fact, it is always easy to find an upper limit of the order of I for any known finite group, as this order cannot exceed the number of different ways in which a set of generating operators may be selected, and hence it can certainly never exceed (g-1)!, g being the order of the group. It is easy to see that there are only three groups for which I has this maximal order, viz. the four-group and the groups of order 2 and 3. Assuming that 0! = 1, the identity might also be classed among these groups. In most cases it is easy to find

much lower upper limits for the order of I.

### § 2. The Groups whose Degree is less than Six.

There is only one group of degree 2, and its group of isomorphisms (I) is the identity. One of the two groups of degree three is the cyclic group of order 3 and hence has the group of order 2 for its I, while the other is symmetric and therefore is simply isomorphic with its I. Two of the groups of degree 4 are cyclic. As their orders are 2 and 4, their I's are the identity and the group of order 2 respectively. Two others are simply isomorphic with the four-group, and hence have the symmetric group of order 6 for their I. A third set of two groups of degree 4 is composed of the alternating and the symmetric groups. These have the symmetric group

of order 24 for their I, according to the well-known theorem quoted above. The seventh and last group of degree 4 is the octic group which is known to be its own I group. The orders of the groups of isomorphisms of the 7 substitution

groups of degree 4 are therefore 1, 2, 6, 8, 24.

The orders of the two cyclic groups of degree 5 are 5 and 6 respectively, and hence their I's are the cyclic groups of orders 4 and 2. Since the group of order 12 and degree 5 is the direct product of the symmetric group of order 6 and the group of order 2 it is simply isomorphic with its I, according to theorem IV. This is also true of the non-cyclic group of order 6, as this is simply isomorphic with the symmetric group of this order. The metacyclic and the semi-metacyclic groups of orders 20 and 10 repectively are known to have the former for their I, while the alternating and the symmetric groups have the latter for their common I. Hence the orders of the groups of isomorphisms of the 8 substitution groups of degree 5 are 2, 4, 6, 12, 20, 120.

# § 3. The Groups of Degree Six.

In the preceding section we considered all the possible abstract groups whose order is less than 7, and hence we know the groups of isomorphisms of the 9 substitution groups of degree 6 whose orders do not exceed their degree. There are ten other groups of this degree which are simply isomorphic with groups of lower degree, viz. three of order 8, two of order 12, three of order 24, and one of each of the orders 60 and 120. Hence only 18 of the 37 groups of degree 6 are distinct, as abstract groups, from those of lower degrees. Two of these 18 are simply isomorphic with the group of order 8 which contains 7 operators of order 2, and hence have the simple group of order 168 for their I. The remaining group of order 8, (abcd)cyc.(et)), is of type (2, 1), and hence has the octic group for its I. The group of order 9 is of type (1, 1), and hence has the transitive group of degree 8 and order 48 which involves operators of order 8 as its I. Since the group of order 16 is the direct product of the octic group and the group of order 2, its I is known \* to be the transitive group of degree 8 and order 64 which Cayley denoted by

# (ae.bf.cg.dh)N $\{(abcd)_8(efgh)_8\}$ dim.

The group of order 18, which is the direct product of the

<sup>\*</sup> Quarterly Journal of Mathematics, vol. xxviii. (1896) p. 252.

symmetric group of order 6 and the group of order 3, has for its I the direct product of the symmetric group of order 6 and the group of order 2, according to the theorem; if a group is generated by two characteristic subgroups which have only the identity in common, its I is the direct product of the I's of these characteristic subgroups. Since the other group of order 18 is obtained by extending the group of order 9 and of type (1, 1) by means of an operator of order 2 which transforms each of its operators into its inverse, its I is the holomorph of this group of order 9 and hence is the doubly transitive group of degree 9 and order 432, according to the theorem given above. The two groups of order 24 which are not simply isomorphic with the groups of lower degrees are the direct products of the alternating group of order 12 and the group of order 2. As these factors are characteristic subgroups of this direct product, its I is the symmetric group of order 24.

Two of the groups of order 36 are simply isomorphic with the square of the symmetric group of order 6, and hence have the double holomorph of this symmetric group for their I. This double holomorph is the group of order 72 and degree 6. The other group of order 36 is a characteristic subgroup of this double holomorph and the order of its I cannot be less than 144, which is the order of the I of this double holomorph, as we shall soon prove. Since this group of order 36 is generated by two operators of orders 3 and 4 respectively, and as the former of these operators could not be selected in more than 8 ways while the latter may be selected in no more than 18 ways, it follows that the order of this I is 144 if the order of the I of the given double holomorph is 144. When we prove the latter fact we shall also prove that this group of order 36 and the group of order 72 and of degree 6 have the same I.

Since the groups of order 48 are the direct product of the symmetric group of order 24 and the group of order 2, they are simply isomorphic with their I. The group of order 72 contains subgroups of order 12 and degree 6 which give rise to a transitive representation, and hence it admits outer isomorphisms according to the given theorem. Moreover, it contains a characteristic subgroup of order 36 which does not admit more than 144 holomorphisms. The holomorphism of the group of order 72 is fixed by that of this subgroup, since the former contains only one operator of order 2 which is commutative with every operator of a subgroup of order 6 contained in the latter. Hence each of these groups has the same I and its order is 144. If this group of order 144 is

represented as a transitive substitution group of degree 12 with respect to a subgroup in the given group of order 72, the two sets of 6 subgroups of order 12 will correspond to two systems of imprimitivity. Hence there are two transitive groups of degree 12 and order 144 whose heads are obtained by making the group of degree 6 and order 72 simply isomorphic with itself, while the published list of these groups gives only one \*. As it is well known that the I of the alternating and the symmetric group of degree 6 may be represented as an imprimitive group of degree 12 and order 1440 t. it has been proved that the substitution groups of degree 6 which cannot be represented as substitution groups of lower degrees have groups of isomorphisms of the following orders: 168, 8, 48, 64, 12, 432, 24, 72, 144, 1440. The two groups of order 48 are clearly distinct, as one involves operators of order 8 while the other does not have this property. The 13 distinct abstract groups which may be represented as substitution groups of degree 6, but of no lower degree, have therefore 11 distinct groups of isomorphisms.

# § 4. The Groups of Degree Seven.

Only eleven of the forty groups of degree 7 are simply isomorphic with groups of lower degrees. Three others are simply isomorphic with the cyclic groups of orders 7, 10, 12 respectively, and hence they have for their I's the cyclic groups of orders 6 and 4, and the four-group. Two of the remaining three groups of order 12 are simply isomorphic with the direct product of the four-group and the group of order 3, and hence their I is the direct product of the symmetric group of order 6 and the group of order 2. This is also the I of the other non-cyclic group of order 12 which is not simply isomorphic with groups of lower degrees, since the holomorph of the cyclic group of order 6 is the direct product of the symmetric group of order 6 and the group of order 2. We have now considered the I's of the 5 possible abstract groups of order 12, and found that their orders are 4, 12, and 24 respectively. Three of these groups have the holomorph of the cyclic group of order 6 for their 1.

The three groups of orders 14, 21, and 42 have the last of

<sup>\*</sup> Quarterly Journal of Mathematics, vol. xxviii. (1896) p. 223. † Bulletin of the American Mathematical Society, vol. i. (1895) p. 258.

these for their I, since the metacyclic group of order p (p 1) and degree p, p being any odd prime, is the group of isomorphisms of all its subgroups whose orders are divisible by p and exceed p. The group of order 20 has the direct product of the group of this order and of degree 5 and the group of order 2 for its I, according to theorem I. The two groups of order 24 which are the direct product of the symmetric group of order 6 and the four-group may be obtained by extending the direct product of the four-group and the cyclic group of order 3 by means of an operator of order 2 which transforms each operator of this direct product into its inverse. Hence by the theorem given above, these groups have the holomorph of this direct product for their I. The order of this holomorph is 144. The group which is the direct product of the cyclic group of order 4 and the symmetric group of order 6 is invariant under the holomorph of the cyclic group of order 12, and has the group of cogredient isomorphisms of this holomorph for its I. Hence the order of this I is 24, and it is the direct product of the symmetric group of order 6 and the four-group.

The direct product of the octic group and the group of order 3 has these two groups for characteristic subgroups, and hence its I is the direct product of the octic and the group of order 2, while the I of the dihedral group of order 24 is the holomorph of the cyclic group of order 12. The orders of these two I's are 14 and 48 respectively. It

remains to consider the I of the group denoted by

# {(abcd)<sub>8</sub> com. (efg) all }dim.\*

As this is invariant under the direct product of the octic and the symmetric group of order 6, and only two operators of this product are commutative with each of its operators, its I is the group of cogredient isomorphisms of this direct product. This I is the direct product of the dihedral group of order 12 and the group of order 2. We have now considered the five types of groups of order 24 which can be represented as substitution groups of degree 7 but not of a lower degree. The orders of their I's are 144, 24, 48, 16. The two I's of order 24 are simply isomorphic.

The group of order 36 contains three invariant tetrahedral groups. As each of these may be transformed into itself by the symmetric group of order 24, the I of the group of order 36 contains this symmetric group invariantly and is

<sup>\*</sup> American Journal of Mathematics, vol. xxi. (1899) p. 328.

the direct product of the symmetric groups of orders 6 and 24 respectively. The group of order 40 is simply isomorphic with its I, since it is the direct product of the group of order 2 and a complete group which involves only one subgroup of half its order. The group of order 48 contains a characteristic subgroup of order 8 and two invariant subgroups of order 6. From these subgroups it follows that the order of its I is 96, and this I is the direct product of this group of

order 48 and the group of order 2.

Since two of the groups of order 72 are direct products of characteristic subgroups, their I's are the direct products of the groups of isomorphisms of these subgroups. orders of these I's are 48 and 144 respectively. maining group of order 72 involves three invariant tetrahedral groups and contains all the operators of its I which transform each of these invariant subgroups into itself. these subgroups are transformed according to the symmetric group of order 6 by I, it follows that the order of this group of isomorphisms is 432. With respect to the characteristic abelian subgroup of order 12, it is isomorphic to the direct product of two symmetric groups of order 6, since the group of cogredient isomorphisms is isomorphic with the symmetric group of order 6 with respect to the same subgroup and does not permute the given three tetrahedral groups.

The group of order 120 is the direct product of two characteristic subgroups, and its I is the symmetric group of order 120. Since the group of order 144 is the direct product of two characteristic subgroups which are also complete groups, it is simply isomorphic with its I. The simple group of order 168 is known to have the group of degree 8 and order 336 for its I, while the group of order 240 is simply isomorphic with its I, according to the given theorem. The remaining two groups are the alternating and the symmetric, and hence have the latter for their common I. Hence the groups of isomorphisms of the 29 groups, which may be represented on seven but on no smaller number of letters, have the following orders: 4, 6, 12, 42, 40, 144, 24, 48, 16, 96,

432, 120, 336, 240, 5040.

University of Illinois.

XX. On Induced Stability. By Andrew Stephenson.\*

THE conditions under which an imposed periodic change in the spring of an oscillation exerts a cumulative effect in magnifying the motion, have already been investigated †. We shall now examine the influence of such a variation on instability of equilibrium and, in certain cases, of steady motion.

The equation of motion about statically unstable equilibrium

under variable spring is

$$\ddot{x} - (\mu^2 - 2\alpha n^2 \cos nt)x = 0,$$

and the complete solution is given by

$$x = \sum_{-\infty}^{\infty} A_r \sin \{(c-rn)t + \epsilon\},$$

where

$$-A_r\{\mu^2 + (c-rn)^2\} + \alpha n^2(A_{r-1} + A_{r+1}) = 0. \quad . \quad (r)$$

In the limit when k, taken positive, is infinite

$$\mathbf{A}_{\pm k} = \frac{\mathbf{\alpha}}{k^2} \mathbf{A}_{\pm (k-1)},$$

so that the series is convergent in both directions. If the eliminant of the equations (r) gives a real value for c, the elementary oscillations are of constant amplitude and the equilibrium is stable.

An approximation  $\ddagger$  for c is readily obtained when  $\alpha$  is

small, for in that case, r being positive,

$$\mathbf{A}_{\pm r} = \frac{\alpha n^2}{\mu^2 + (c \mp rn)^2} \mathbf{A}_{\pm (r-1)}$$

approximately, and on substituting for  $A_1$  and  $A_{-1}$  in (0) we find that for a real c when  $\alpha$  is small n must be large compared with  $\mu$ : then

 $c^2 = 2\alpha^2 n^2 - \mu^2,$ 

and for stability n must be greater than  $\mu/\alpha\sqrt{2}$ .

Thus the system can always be maintained about a position of otherwise unstable equilibrium by a periodic variation in spring of sufficiently large frequency. The inverted pendulum, for example, is rendered stable by rapid vertical

\* Communicated by the Author.

‡ Similar to that employed in the former of the two papers referred

to above.

<sup>† &</sup>quot;On a class of forced oscillations," Quarterly Journal of Mathematics, no. 168, 1906. "On the forcing of oscillations by disturbances of different frequencies," Phil. Mag. July 1907.

vibration of the point of support. The above analysis shows that quite apart from gravity, an imposed motion of small amplitude and high frequency produces a comparatively slow simple oscillation about its own direction; the impressed action must therefore exert a restoring moment on the body proportional to the displacement of the mass centre from the line of the applied motion, and if this moment numerically exceeds the outward moment due to gravity stability is ensured \*.

If the pivot is given a simple vibration of amplitude a with frequency n per  $2\pi$  seconds, the equation of motion about the unstable position is

$$\ddot{x} - \frac{h}{k^2} (g - an^2 \cos nt) x = 0.$$

For a simple pendulum 1 metre long  $\mu^2=10$  approximately, and if a=10 cm. for stability n>44.7; thus a frequency of 7.2 per second is sufficient to maintain relative equilibrium. If the pendulum is 20 cm. in length  $\mu^2=50$ , and if a=10 the condition would give n>20, a frequency of over 3.2 per second. In this case, however,  $\mu/n$  is not sufficiently small for the approximate formula to be applicable.

There is no difficulty in verifying the stability under the imposed motion by experiment. It is found furthermore that the pendulum may be rendered approximately steady in a position sensibly oblique by a comparatively small inclination of the direction of vibration, and it is of interest to enquire under what circumstances this occurs.

If the path of the pivot makes a small angle  $\beta$  with the vertical the equation of motion is

$$\ddot{x} - \frac{h}{k^2}(g - an^2 \cos nt) x = \beta \frac{h}{k^2} an^2 \cos nt.$$

For the particular solution giving the forced motion due to the disturbance represented by the term on the right, we have

$$x = \sum_{0}^{\infty} \mathbf{B}_{r} \cos rnt,$$

where

$$-B_r \left(\frac{gh}{k^2} + r^2n^2\right) + \frac{1}{2}\frac{ha}{k^2}n^2(B_{r-1} + B_{r+1}) = 0, \quad . \quad (r)'$$

\* The stability of this particular system is worked out from first principles for a special case in a paper "On a new type of dynamical stability," read before the Manchester Literary and Philosophical Society in January 1908.

except for r=0 and 1, for which

$$-B_0 \frac{gh}{k^2} + \frac{ha}{k^2} n^2 B_1 = 0, \dots (0)$$

and

$$-B_{1}\left(\frac{gh}{k^{2}}+n^{2}\right)+\frac{1}{2}\frac{ha}{k^{2}}n^{2}(2B_{0}+B_{2})=\beta\frac{ha}{k^{2}}n^{2}. \quad . \quad (1)^{4}$$

The series is evidently convergent. Since  $\frac{gh}{k^2} = \mu^2$  is small compared with  $n^2$ ,

$$\mathbf{B}_r = \frac{1}{r^2} \cdot \frac{ah}{k^2} \mathbf{B}_{r-1}$$

approximately if r > 1.

Also  $B_1 = \frac{2g}{an^2}B_0$ , and therefore  $B_2 = \frac{1}{2}\frac{gh}{k^2n^2}B_0$ .

 $\mathbf{B}_2$  is therefore negligible in (1)', and finally

$$B_0 = \frac{\beta}{1 - \frac{2gk^2}{n^2a^2h}}.$$

As before for the stability of the "free" motion  $n^2$  must exceed  $\mu^2/2\alpha$ , which is equal to  $2gk^2/a^2h$ : if, therefore, n is in the vicinity of this limit  $B_0$ , the mean inclination of the pendulum, is large compared with  $\beta$ , the inclination of the path of the pivot. Since  $2g/an^2$  is small, being less than  $ah/k^2$ , it is clear that  $B_0$  is large compared with  $\sum_{i=1}^{\infty} |B_r|$ ; i. e.,

the forced oscillation about the inclined position is comparatively small. This fact is very evident experimentally.

As n increases  $B_0$  decreases to the limit  $\beta$ , and the rod approaches the line of vibration.

2. A case of steady motion for which the stability equation is of the type

$$\ddot{x} + \lambda x = 0$$

is furnished by a solid of revolution rolling on a horizontal plane. Consider the rectilinear motion of such a body symmetrical about the middle plane normal to its axis. The small oscillations are determined by

$$(A + Mb^2)\ddot{x} + \{Cp^2(C + Mb^2)/A - (b - \rho)Mg\}x = 0,$$

where p is the angular velocity, b the radius of the midsection,  $\rho$  the other principal radius at any point on it, and the other constants are in the usual notation.

When, therefore,  $p^2 < g \frac{(b-\rho)MA}{C(C+Mb^2)}$  the motion is unstable.

If now the plane is given a simple oscillation vertically, g must be replaced in the above equation by  $g + an^2 \cos nt$ , and the motion is rendered stable if

$$2\left\{\frac{1}{2}\frac{(b-\rho)\mathbf{M}}{\mathbf{A}+\mathbf{M}b^2}a\right\}^2n^2 > \frac{\mathbf{C}(\mathbf{C}+\mathbf{M}b^2)}{\mathbf{A}(\mathbf{A}+\mathbf{M}b^2)}\left\{\frac{g(b-\rho)\mathbf{M}\mathbf{A}}{\mathbf{C}(\mathbf{C}+\mathbf{M}b^2)} - p^2\right\},$$

where, as before, in making the approximation it is assumed that  $\frac{(b-\rho M)}{A+Mb^2}a$  is small. The range of action is limited by the conditions of the problem which require that  $an^2$  must

not exceed g.

3. In general the single equation determining the oscillations of a system about steady motion is of order higher than the second, as for example in the case of the spinning top, which we now examine in the present connexion. The unstable position of equilibrium of a symmetrical top may be rendered stable either by an axial spin or by an imposed vertical vibration of the point of support. The two actions together might therefore be expected to reinforce one another, if either singly is not of sufficient intensity.

For the small oscillations about the position of equilibrium

$$\ddot{x} - p\dot{y} - (\mu^2 - 2\alpha n^2 \cos nt)x = 0$$
  
$$\ddot{y} + p\dot{x} - (\mu^2 - 2\alpha n^2 \cos nt)y = 0,$$

and a solution is

$$\begin{split} x &= \sum_{-\infty}^{\infty} \mathbf{A}_r \sin \left\{ (c - rn)t + \epsilon \right\}, \\ y &= \sum_{-\infty}^{\infty} \mathbf{A}_r \cos \left\{ (c - rn)t + \epsilon \right\}, \end{split}$$

where

$$-\{\mu^2 + (c-rn)^2 - p(c-rn)\}A_r + \alpha n^2(A_{r-1} + A_{r+1}) = 0,$$

This set of conditional equations is similar to the system (r) in § 1, and admits of corresponding approximate treatment. If  $\alpha$  is small and n is large compared with  $\mu$  and p, we find

$$\mu^2 + c^2 - pc - 2\alpha^2 n^2 = 0,$$

and therefore for stability in this case

$$2\alpha^2 n^2 > \mu^2 - \frac{1}{4}p^2$$
.

Thus when the imposed motion is comparatively rapid the two actions are simply cumulative.

Manchester, October 1907.

# XXI. A Freehand Graphic way of determining Stream Lines and Equipotentials. By L. F. RICHARDSON \*.

#### Plate XII.

#### SCHEME OF PAPER.

I. On the need for new methods.

II. The first idea of freehand solution and confirmation of its accuracy.

III. The conditions which the solution of  $\nabla^2 V = 0$  must satisfy in order that it may be determinable by a single graph.

(a) When the guiding lines are normal to a family of surfaces.

Possible types—test cases.

(b) Thin shells.

(c) Screw symmetry—example.

IV. Points and lines of equilibrium.V. Equations other than Laplace's—variable conductivity.

VI. Boundary conditions.

VII. Miscellaneous notes on draughtsmanship. VIII. Estimation of errors.

### I. The Need for New Methods.

# HE Laplacian differential equation

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = 0$$

has received an extraordinary amount of attention during the last century owing to the great number of physical quantities, the space distribution of which can be determined from its integrals. The analytical integrals hitherto obtained by such means as Fourier series, Bessel functions, spherical and other harmonics make it possible to determine the distribution when the boundary conditions bear relation to certain simple types of surface, such as parallelipipeds, cylinders, spheres, ellipsoids, anchor rings, &c.

Now for physical research this is well enough. usually possible to arrange the instruments so that the parts involved are of these simple forms. The wires may be wound in circular rings of small cross-section, as in Helmholtz's galvanometer. The pieces of substance for the measurement of specific properties may be shaped into square bars, as in Forbes's experiments on the flow of heat. Or, as in Kelvin's

<sup>\*</sup> Communicated by the Physical Society; read November 8, 1907. Phil. Mag. S. 6. Vol. 15. No. 86. Feb. 1908.

attracted disk electrometer, parallel plates may be made

practically infinite by his device of the guard-ring.

But for the purposes of the engineer this is of very limited application. If he is to handle partial differential equations freely, they must be applicable to bodies of most various shapes, such, for example, as the toothed core-plates of dynamos, the water surrounding ship shells and screw propellers, the space between turbine blades, and a host of other forms, too irregular to be readily described.

Further than this, the method of solution must be easier to become skilled in than are the usual methods with harmonic Few have time to spend in learning their And the results must be easy to verify—much mysteries. easier than is the case with a complicated piece of algebra. Moreover, the time required to arrive at the desired result by analytical methods cannot be foreseen with any certainty. It may come out in a morning, it may be unfinished at the end of a month. It is no wonder that the practical engineer is shy of anything so risky.

Harmonic functions have, however, one very strong point in comparison to the methods put forward in this paper, and that is their accuracy. Once we have determined V as an infinite series of harmonic functions, it is usually not much more labour to obtain an accuracy of 1 in a million than of

1 in ten.

Now it is true that in the determination of absolute electric standards measurements are made to 1 in 100,000 or to an even greater refinement. But for most chemical and physical work 1 in 1000 is more like the limit attained. And in any new branch of research, two, five, or even ten per cent. are very welcome. The root of the matter is that the greatest stimulus of scientific discovery are its practical applications. And here, in the design of machinery for example, cost rules everything, and this can seldom be foreseen as near as 1 per cent.

To sum up. The existing methods of solving Laplace's equation are susceptible of great accuracy, but they are slow and uncertain in time and, most serious of all, they can only be applied to very special boundary conditions. obviously a demand for a method of solving that group of partial differential equations - of which we may regard Laplace's as the simplest type—which shall, if necessary, sacrifice accuracy above 1 per cent., to rapidity, freedom from the danger of large blunders, and applicability to more various forms of boundary surface.

### II. The First Idea of Freehand Solution.

The real simplicity of the space distributions of electric and magnetic phenomena,—so much disguised in the algebraic integrals of the differential equations, but rescued from confusion and clearly set forth by the vector analysts, Heaviside, Walker and others,—leads one to hope for equally simple methods of calculating their numerical values with reference to any boundary whatever.

The beautiful figures of stream and equipotential surfaces published by Maxwell, Lamb and others as the result of harmonic analysis, and by Hele Shaw as the result of experiment, suggest that by imitating their characteristic properties freehand we may, in some small part, attain the result

desired.

Maxwell in § 92 of his 'Elementary Treatise on Electricity and Magnetism' speaks of tentative methods of altering known solutions of the Laplacian equation by drawing diagrams on paper and selecting the least improbable. The object of the present thesis is to point out that this method can do far more than merely alter known results, and that it may be so far from tentative as to yield an accuracy of one per cent of the range.

This method of treating potentials, although still far from combining all desirable qualities, and suffering from the restriction to certain types of symmetry, yet from its great freedom within those types may, it is hoped, supply to a

certain extent the demand we have indicated.

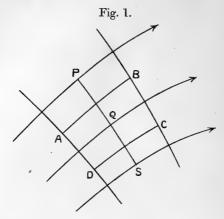
On turning to Maxwell's figures and picking out those in which V is independent of z so that we have

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} = 0,$$

it will be seen that while the curves are of the most various shapes yet the chequerwork of all the diagrams possesses these two properties in common:—(1) the corners are orthogonal, (2) when the chequers are small enough the ratio of their length to breadth is the same in all parts of the field.

The proof of this follows most conveniently from the consideration of the motion of a liquid when the lines of flow lie in parallel planes and the motion is the same at all points of any normal to these planes. Draw three adjacent stream lines defining two adjacent tubes of flow.

Take two points A and B on the mid line of one tube, and from A and B draw normals to the direction of flow cutting the mid line of the other tube in D and C respectively.



Halfway between AD and BC draw a line PQS normal to the direction of flow so that PQ is the width of one tube and QS of the other. Now if the fluid is incompressible and we have drawn the tubes so that the flow in each is the same, then the respective velocities are to one another inversely as

PQ and QS. Let the velocities be  $\frac{k}{PQ}$  and  $\frac{k}{QS}$ . Next let

us take the line integral of the velocity round the small rectangle ABCD. The sides AD and CB are normal to the flow and so contribute nothing. The sides AB and CD contribute

$$AB \times \frac{k}{PQ} - \frac{DC \times k}{QS} = k \left\{ \frac{AB}{PQ} - \frac{DC}{QS} \right\}.$$

Now  $\frac{AB}{PQ}$  is the ratio of the length along the flow to the breadth across the flow of the small chequer which has A, Q, B, P, at the mid points of its four sides. It will be convenient to have a special name for this quantity, and I propose to call it the "chequer ratio" with the understanding that length along the flow is always in the numerator, and that the chequer is so small that its size no longer causes an appreciable deviation from the accuracy obtained by using infinitesimals. Then we have:—

Line integral of the velocity around ABCD= $k \times \begin{cases} \text{Difference between successive } \\ \text{chequer ratios in a direction } \\ \text{perpendicularly across flow.} \end{cases}$ 

Now the curl of the vector velocity is defined as the line integral round a small circuit divided by the area of that circuit—that is in this case by the area ABCD which will in the limit be equal to the mean of the areas of the two adjacent chequers. So that we have:—

 $\begin{array}{c} \text{difference of successive chequer ratios in a direction} \\ \text{curl of the velocity} = k & \begin{array}{c} \text{perpendicular to velocity} \\ \hline \text{mean chequer area} \end{array}$ 

If the velocity has no curl the chequer ratio must not vary along any line normal to the flow. It may vary from one normal to another, but if on the other hand we prefer to make it constant all over the field, then at any point the distance between successive normals will be inversely as the flow, so that these normals will be contours drawn at equal intervals of a velocity potential.

To return: since the fluid is incompressible the condition for the existence of a stream function is satisfied, and since the stream-lines are drawn so that the flow between each successive pair is the same, it follows that these stream-lines are the contours drawn at equal intervals of a stream function  $\psi$ . Now it is proved in works on Hydrodynamics

that  $\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2}$  is equal to the curl of the vector velocity. Therefore:—

$$\frac{\eth^2 \psi}{\eth x^2} + \frac{\eth^2 \psi}{\eth y^2} = k \frac{\text{difference of successive chequer ratios in a direction}}{\text{mean chequer area}}.$$

And since  $\psi$  may be any one-valued function of position on the plane, it is seen that all hydrokinetical considerations have been eliminated from the above equation, which is purely a proposition in differential geometry. The only implication being that contours are drawn at equal intervals of  $\psi$  whatever be its physical meaning.

To draw chequers freehand so as to satisfy a difference relation of this sort between the chequer ratios is likely to be toilsome, and we will here consider only the case when  $\nabla^2 \psi = 0$ .

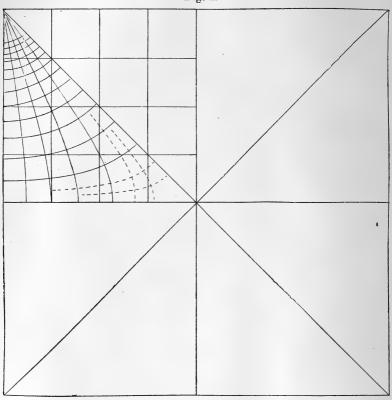
Supposing then that a chequerwork has been obtained in which the chequer ratio is everywhere the same and in which the given boundary conditions are satisfied, then by the

uniqueness of the solution of  $\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} = 0$  this chequerwork gives us what we want.

# 242 Mr. L. F. Richardson on a Freehand Graphic way

It remains to be shown what accuracy may be expected from the freehand method. This is of course largely a personal matter. I exhibit my own handiwork. Others will doubtless obtain greater precision. Throughout this paper I have chosen test cases in which the analytical verification should not be too difficult. Hence the diagrams look rather stiff and formal and do not in any way do justice to the freedom of this graphic method.

Fig. 2.



Example of the solution of  $\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} = 0$ .—Along one pair of opposite edges of a square V = 1, along the other pair V = 0. Find V at all points inside. By symmetry V will be equal to  $\frac{1}{2}$  along the diagonals. And again by symmetry, the lines joining mid-points of opposite sides will be normal to the contours of V. So that it is only necessary to find V in half one-quarter of the square. Further, by symmetry, at a

corner of the square the contours drawn at equal intervals of V must make equal angles with one another. One starts then by ruling out an accurate square, putting in the diagonals, joining the mid-points of its sides and setting off the equal angles with a protractor. It is convenient to divide the range of V into ten equal parts. Having thus prepared the paper, lines were sketched and amended until further improvement became very slow. The pencil-lines were then firmly fixed in ink. Coordinate lines were drawn in and the values of V at six points were read from the diagram and are given in parenthesis in the accompanying table. The whole work from the beginning of the drawing took two or three hours.

				•5
			•5	(·47) ·466
1:0		•5	(·40) ·396	(.365)
1.0	•5	(·307)	(.23)	(·20)
•5	0	0	0	0

Not until this had been done did I look up the correct values which had been computed from the analytical solution

$$V = \frac{4}{\Pi} \sum_{m \text{ odd}} (-1)^{\frac{m-1}{2}} \frac{1}{m} \operatorname{sech} \frac{m\Pi}{2} \cos mx \cdot \cosh mz.$$

These are given in the table beside the numbers read from the graph. From these we find the errors +.007, +.007, -.002, +.004, +.001, +.004. Treating these as all of the same sign, their mean is .0042.

The error of a graph may well be compared with the total range of V within which the determination was made freehand. In this case the range was 0.5 so that the mean

error was 0.84 per cent. of the range, a degree of accuracy

which would be sufficient for many purposes.

Having shown that the freehand method is a practical one in a plane, it will be well next to enquire to what types of symmetry it may be extended.

# III. Possible Types of Symmetry.

Inasmuch as a single chequerwork is to determine the distribution in the whole of the space considered, we are confined to two coordinates. The freehand method at present offers nothing to compete with the analytic forms in which three coordinates appear, such as:

$$\mathbf{V} = \sum_{m,n} (\mathbf{A}_m \sin mx + \mathbf{B}_m \cos mx) (\mathbf{C}_n \sin ny + \mathbf{D}_n \cos ny) (\mathbf{F} e^{-\sqrt{m^2 + n^2} \cdot z} + \mathbf{G} e^{+\sqrt{m^2 + n^2} \cdot z})$$

$$\mathbf{V} = \sum_{m,k} e^{\pm kz} (\mathbf{A}_m \cos m\phi + \mathbf{B}_m \sin m\phi) \mathbf{J}_m(kr),$$

(Whittaker, 'Modern Analysis,' p. 318)

$$V = \sum_{n, m} C_m r^m (A_n \cos n\phi + B_n \sin n\phi) (\sin \theta)^n \cdot \frac{d^n P_m \mu}{d\mu^n},$$
(Byerly, 'Fourier's Series,' p. 196)

or others like them.

The expressibility of V in terms of two coordinates implies that V is constant along a certain family of lines in space, namely, the intersections of the surfaces over which the said two coordinates are respectively constant. Any particular type of symmetry is most conveniently distinguished by specifying the family of lines along each of which V must be constant.

As it will frequently be necessary to refer to these lines and to distinguish them from the normals to the surfaces V=constant, I propose to call them the "guiding lines."

It is indeed conceivable that by adding together several space distributions in each of which V is constant along a different family of lines, we might attempt the solution of problems which it may be impossible to treat by two coordinates directly, such for example as the motion of a perfect fluid past a three-bladed screw-propeller, or the electrostatic field due to a ring of electrons. It may even be possible to treat the most general distributions by means of sections of the potential surfaces drawn on the leaves of a book of tracingpaper. But these extensions must be left to those who desire the results. This paper deals only with two coordinates.

Case (a). The guiding lines are everywhere orthogonal to a family of surfaces.—Let these be the surfaces over each of

which  $\gamma = F_3(x, y, z)$  is constant.

Then choosing a particular surface, say  $\gamma = \gamma_0$ , we wish to draw thereon a chequerwork of orthogonal lines, and we wish this chequerwork, by the motion of each point of it along the guiding line at that point, to sweep out two families of surfaces in space, in such a way that one family may be equipotentials and the other stream surfaces. This requires that these two families, which we may denote by

$$\alpha = F_1(x, y, z) = \text{const.}, \qquad \beta = F_3(x, y, z) = \text{const.},$$

should be everywhere orthogonal. Therefore the surfaces  $\alpha$ ,  $\beta$ ,  $\gamma$  are mutual orthogonal, and consequently the surfaces  $\gamma$  must satisfy the condition necessary in any member of a triply orthogonal system (Salmon, 'Geometry of Three Dimensions,'

4th ed. §§ 476 to 486).

But more than this. For we wish to be unrestricted as to the direction of the orthogonal traces of  $\alpha$  and  $\beta$  drawn upon the surfaces y. Therefore, since three mutually orthogonal surfaces necessarily intersect in their lines of curvature (loc. cit. § 304), it follows that at every point of the surfaces γ there are lines of curvature in every direction. The only form which possesses this property is the sphere or its limit the plane. Therefore the surfaces  $\gamma$  are either spheres or planes. This is necessary. We have not proved that it is sufficient. As frequent reference will be made to the theorems proved in Lamé's Leçons sur les coordonnées curvilignes, it will be convenient to employ expressions such as (Lamé, § xi. 15) to indicate equation 15 of § xi. of this treatise. The relation of our notation to Lamé's is that his  $\rho$   $\rho_1$   $\rho_2$  are replaced by  $\alpha \beta \gamma$  and that  $\alpha \beta \gamma$  are used as subscripts respectively instead of absence of subscript, 1 and 2. Otherwise the notations are the same.

In particular, if F is any function of position, we will denote by  $H_F$  the quantity

$$\frac{1}{\sqrt{\left(\frac{\partial F}{\partial x}\right)^2 + \left(\frac{\partial F}{\partial y}\right)^2 + \left(\frac{\partial F}{\partial z}\right)^2}}$$

which is the reciprocal of the space-rate of F along the normal to the surface F = constant.

Consider the lamina bounded by the two spheres  $\gamma$  and  $\gamma + \delta \gamma$ . The thickness of the lamina is  $H_{\gamma} \delta \gamma$ . If  $\alpha = V =$ the

potential, then the surfaces  $\beta$  = constant are surfaces of flow. Denoting in like manner the distances between two adjacent surfaces of these families by  $H_{\alpha}\delta\alpha$ ,  $H_{\beta}\delta\beta$ , we see that  $H_{\alpha}\delta\alpha$  and  $H_{\beta}\delta\beta$  are the length and breadth of a chequer traced on the surface  $\gamma$ .

A tube of flow is bounded by the four surfaces  $\beta$ ,  $\beta + \delta\beta$ ,  $\gamma$ ,  $\gamma + \delta\gamma$ . And its cross section is therefore  $H_{\beta}$ .  $H_{\gamma}$ .  $\delta\beta$ .  $\delta\gamma$ . Now if the flux has no divergence, then along a tube of flow magnitude of flux multiplied by cross-section=constant. But the magnitude of flux is equal to the negative space-rate

of the potential  $\alpha$  along the line of flow, and this is  $-\frac{1}{H_{\alpha}}$ . Therefore along a line of flow  $\frac{H_{\beta}.H_{\gamma}}{H_{\alpha}}\cdot\delta\beta$ .  $\delta\gamma$  must be con-

stant in order that the vector space-rate of the scalar  $\alpha$ —the Hamiltonian  $\nabla \alpha$ —shall have no divergence. Or equivalently the condition that

$$\nabla^2 \alpha = 0$$
 is  $\frac{\partial}{\partial \alpha} \left( \frac{H_{\beta} \cdot H_{\gamma}}{H_{\alpha}} \right) = 0$ .

Now we may by freehand trial and amendment so arrange the orthogonal lines on the surface  $\gamma_0$  that the above relation shall hold true on the surface  $\gamma_0$ ; but we must further enquire what conditions the spheres  $\gamma$  must satisfy in order that  $\frac{\partial}{\partial \alpha} \left( \frac{H_{\beta} \cdot H_{\gamma}}{H_{\alpha}} \right) = 0$  shall be true for all values of  $\gamma$  when it is true for one  $\gamma_0$ ; and this moreover when  $\alpha$  and  $\beta$  are

At this stage the fact that the surfaces  $\gamma$  are spheres makes a remarkable simplification. For supposing for a moment that they did not possess this property and that  $r_{\gamma}^{a}$  and  $r_{\gamma}^{s}$  were their principal radii of curvature at any point, then by (Lamé,  $\S$  xxx. 24)

$$\frac{1}{r_{\gamma}^{a}} = \frac{h_{\gamma}}{h_{a}} \cdot \frac{\partial h_{a}}{\partial \gamma}, \qquad \frac{1}{r_{\gamma}^{\beta}} = \frac{h_{\gamma}}{h_{\beta}} \cdot \frac{\partial h_{\beta}}{\partial \gamma},$$

where  $h_{\alpha} = \frac{1}{H_{\alpha}}$ , and similarly for  $\beta$  and  $\gamma$ . Equating the two curvatures,

otherwise undetermined.

$$h_{\beta} \cdot \frac{\partial h_{\alpha}}{\partial h_{\alpha}} = h_{\alpha} \frac{\partial h_{\beta}}{\partial h_{\beta}}.$$

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Now

$$\frac{\partial}{\partial \gamma} \left( \frac{\mathbf{H}_{\beta}}{\mathbf{H}_{\alpha}} \right) = \frac{\partial}{\partial \gamma} \left( \frac{h_{\alpha}}{h_{\beta}} \right) = \frac{-h_{\alpha} \frac{\partial h_{\beta}}{\partial \gamma} + h_{\beta} \frac{\partial h_{\alpha}}{\partial \gamma}}{h_{\beta}^{2}}$$

and therefore vanishes; so that the chequer ratio  $\frac{H_{\alpha}}{H_{\beta}}$  is a function of  $\alpha$  and  $\beta$  only.

As has already been stated, to make  $\nabla^2 \alpha = 0$  on the surface  $\gamma_0$  we must have

$$\frac{\partial^{\alpha}}{\partial \alpha} \left( \frac{H_{\beta} H_{\gamma_0}}{H_{\alpha}} \right) = 0,$$

which may conveniently be arranged by making

$$\frac{\mathbf{H}_a}{\mathbf{H}_B} = k_0 \mathbf{H}_{\mathbf{y}_0}$$

where  $k_0$  is a constant, so that the chequer ratio is given as a function of position on  $\gamma_0$ . This is more than sufficient in that it makes

$$\frac{98}{9} \Big( \frac{\mathrm{H}^{\alpha}}{\mathrm{H}^{\alpha}} \Big)$$

vanish as well, but the loss of generality involved is found not to matter, while the simplicity gained is a great con-Next, because  $\frac{H_a}{H_B}$  is independent of  $\gamma$  it follows venience. that on any other surface  $\gamma_1$  we still have

$$\frac{\mathbf{H}_a}{\mathbf{H}_B} = k_0 \, \mathbf{H}_{\gamma_0}.$$

But if  $\nabla^2 \alpha = 0$  is to be satisfied on this second surface we must there have

$$\frac{\mathbf{H}^a}{\mathbf{H}_{\beta}} = k_1 \, \mathbf{H}_{\gamma},$$

where  $k_1$  is a second constant. Therefore regarding  $\gamma_0$  as fixed and  $\gamma_1 = \gamma$  as movable we have  $H_{\gamma} = H_{\gamma_0} \times a$  function of y only.

But  $H_{\gamma_0}$  is a function of  $\alpha$  and  $\beta$  only. This relation is equivalently expressed by the two equations

$$\frac{\partial^2}{\partial \gamma \partial \alpha} (\log H_{\gamma}) = 0, \quad \frac{\partial^2}{\partial \gamma \partial \beta} (\log H_{\gamma}) = 0,$$

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$$\frac{\partial}{\partial \gamma} \left( \frac{1}{h_{\alpha} r_{\alpha}^{\gamma}} \right) = 0, \qquad \frac{\partial}{\partial \gamma} \left( \frac{1}{h_{\beta} r_{\beta}^{\gamma}} \right) = 0.$$

But if the surfaces γ are planes, then by the equations (Lamé, § xxx. 24) already quoted

$$\frac{\partial \gamma}{\partial \gamma} \left( \frac{1}{h_{\alpha}} \right) = 0 = \frac{\partial \gamma}{\partial \gamma} \left( \frac{1}{h_{\beta}} \right)$$

and consequently  $\frac{1}{r_a{}^{\gamma}}$  and  $\frac{1}{r_{\beta}{}^{\gamma}}$  are independent of  $\gamma$ . But it is shown by Lamé (§ xxxviii.) that the curvature of the arc of intersection of the surfaces  $\alpha$  and  $\beta$  is equal to

$$\sqrt{\left(\frac{1}{r_a^{\gamma}}\right)^2 + \left(\frac{1}{r_{\beta}^{\gamma}}\right)^2}$$
.

So that if the radius of curvature of this arc be p then p is independent of  $\gamma$ . But p is equal to the length of the normal from the point considered onto the line of ultimate intersection of two consecutive planes of the family  $\gamma$  which pass one on either side of the point considered. As the plane moves this length must remain constant. And as this is to be true for every point in space, it is easy to see that if the surfaces  $\gamma$  are planes they must intersect in a common axis. We have in this case symmetry about an axis. Or if the axis be at an infinite distance, the planes are parallel, and we have V independent of one of the Cartesian coordinates x, y, z. But if, quite generally, the surfaces  $\gamma$  are spheres

we have only  $\frac{h_a}{h_\beta}$  independent of  $\gamma$  and therefore  $\frac{r_a^{\gamma}}{r_{\beta}^{\gamma}}$  inde-

pendent of  $\gamma$ . If the centres of the spheres  $\gamma$  lie in a straight line, then since the orthogonal traces of the surfaces  $\alpha$  and  $\beta$  on a sphere  $\gamma$  may turn round anyhow, we may choose for  $\beta$  the planes intersecting in the line of the centres of the spheres  $\gamma$ . Then  $r_{\beta}^{\gamma}=0$ , and consequently  $r_{\alpha}^{\gamma}$  is independent of  $\gamma$  so that the traces of  $\alpha$ =const. on the planes  $\beta$  are circles. This is the system of toroidal coordinates which has been treated by Professor Hicks in Phil. Trans. 1881, Part II. Now the above reasoning would lead us to expect in these a type of symmetry which can be dealt with by two coordinates—other than symmetry about an axis. But on referring to Hicks's formulæ it is easy to show that this is not possible for if V be made independent of either of those two of his coordinates which determine position in a plane passing through the axis, then the other of these two will not divide

out of the equation  $\nabla^2 V = 0$ , so that all three coordinates must still be present in the integrals. Clearly then, our deductions, though necessary, are not sufficient. I have little doubt that the omission lies in this: that to leave us unrestricted as to the direction of the orthogonal traces of  $\alpha$  and  $\beta$  upon the surfaces  $\gamma$ , it is not sufficient that the surfaces  $\gamma$  should be spheres. For the curves normal to  $\gamma$  which we have called the "guiding lines" must be such that they form one set of lines of curvature of any surface whatever passing through them. To satisfy this condition it seems likely that except when the radius of the spheres  $\gamma$  is infinite, the guiding lines will have to be straight and the spheres concentric. This is the symmetry when V is independent of the radius in spherical coordinates, but may vary anyhow with the latitude and longitude.

The only case remaining uninvestigated is that in which the surfaces  $\gamma$  are spheres with centres which do not lie on a

straight line.

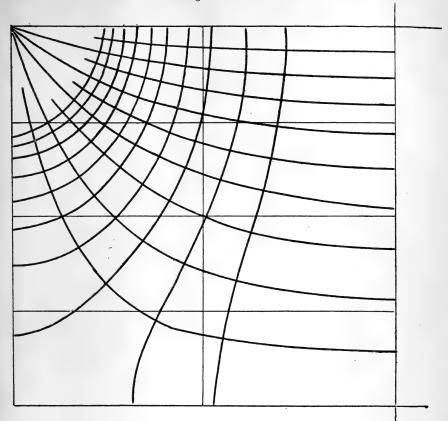
By this application of Lamé's formulæ, aided by those due to Hicks, we have discovered no new type of symmetry which allows two coordinates to be used instead of three. We have proved that within the stated limits the wellknown types are the only possible ones. A summary of these may be useful.

Summary of Types of Symmetry when the guiding lines are orthogonal to a family of surfaces.

Guiding lines.	Chequer ratio.	If $\nabla^2 \mathbf{V}$ is made equal to $f(\mathbf{V}, \alpha, \beta)$ over one surface $\gamma_0$ its value on the others will be	Analytical methods.
Parallel straights.	Constant.	$\nabla^2 \nabla = f(\nabla, \alpha, \beta).$	Conjugate functions.
Circles with their centres on a com- mon axis and their planes nor- mal thereto.		$\nabla^2 \mathbf{V} = f(\mathbf{V}, \alpha, \beta).$	Zonal harmonics of the cylindrical, spherical, spheroidal, and toroidal systems.
Radii from a com- mon point.	Constant.	$\nabla^2 \nabla = \frac{f(\nabla, \alpha, \beta)}{r^2}$ where r is the distance from the radiant point.	

\* Example of Symmetry about an Axis.-Byerly in his 'Fourier's Series and Spherical Harmonics,' p. 230, sets the following problem :- "A cylinder of radius one metre and altitude one metre has its upper surface kept at temperature 100°, and its base and convex surface at the temperature 15°, until the stationary temperature is set up. Find the temperature at points on the axis 25 cm., 50 cm., and 75 cm. from the base, and also at a point 25 cm. from the base and 50 cm. from the axis." To solve this the first thing necessary is to prepare a chart bearing chequers of the appropriate shape for each distance from the axis. The graph of any solution of  $\nabla^2 V = 0$  symmetrical about an axis would serve this purpose. For example several of the figures out of Maxwell's 'Electricity and Magnetism' would do. But I preferred to prepare a standard chart by ruling equidistant parallel equipotentials normal to the axis of revolution, and then stream-lines parallel to the axis at distances from it proportional to the square roots of the natural numbers 0, 1, 2, 3, 4, 5, &c. The cross section of the cylindrical shell enclosed between successive stream-lines is then the same for every pair, and the chequer ratio proportional to the distance from the axis. This having been done in red ink, a sheet of tracing-paper was pinned over it, the section of our given cylinder was drawn in black and equipotentials and lines of flow were drawn in pencil. These were then rubbed out and amended with the aim of making the pencil chequers everywhere very similar to the red rectangles underneath. When improvement became slow, the blurred lines were made firm and definite with ink and the chequers considered individually and marked as to whether they were too square or too thin. The lines were then drawn on a clean sheet of tracing-paper, the chequers again examined individually, and finally the lines fixed in ink (see fig. 3). Coordinate lines were then ruled and the values of V at their intersections were read from the graph. This process, from the ruling in of the given contour to the determination of V in numbers, took me four hours. The analytical method would perhaps have been more rapid in this case; but for an irregular shaped contour with an irregular boundary distribution the freehand solution would still take about the same time, while analytical methods may be almost indefinitely tedious.





The results are tabulated below:-

Distance from base of cylinder	$\begin{array}{c} 25 \\ 0 \end{array}$	50 0	$\begin{array}{c} 75 \\ 0 \end{array}$	25 cms. 50 ,,
naxis name Potential read from the graph as decimal of unit range.	·175	•38	·6 <b>4</b>	•14
Last multiplied by the actual range (100°-15°)	14.9	32.3	54.4	11.9
Last +15°=actual temperature	29.9	47.3	69.4	26.9

Not until these numbers had been written down did I look at the correct values found by Byerly from the Bessel function series, namely:—

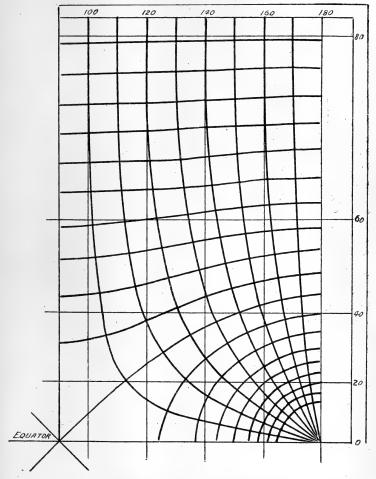
Disregarding signs the mean of these errors is .63 which is equal to 0.74 per cent. of the range of 85°.

Example of the type of symmetry when V is independent of the radius in spherical coordinates.—" On a uniform spherical shell there are equal sources at the north and south poles and equal sinks at the extremities of a diameter lying in the equatorial plane. The sources and sinks send out and receive uniformly in all directions. The flux has no divergence except at the sources and sinks and no curl anywhere. Find the distribution of potential on the surface." Todo this we might draw orthogonal lines on the surface of a globe so as to make the chequers ratio constant. Or because, in Mercator's projection, any small part on the globe transforms into a small part of the same shape on the map, we may transform the boundary conditions and obtain the required solution by drawing chequers of constant chequer ratio on the map. Blank Mercator projections suitable for this work may be obtained from George Philip & Son, Fleet Street. In the present example the lines of flow radiating from the pole become lines straight, parallel and equidistant at infinity. And as the graph progressed it was found that by their symmetry with the sinks on the equator, the foregoing condition must be very nearly satisfied at 10° from the poles, a region which is within the confines of the map. Again, in this case it is only necessary to determine V in one octant of the sphere, and symmetry helps us in other ways. The accompanying graph (fig. 4) is the best of four or five separate attempts. The time taken to make these was collectively four hours. Special attention was given to the equipotential curve which passes mid-way between the two equatorial sinks, and as the result of the aforesaid trials it was found to pass through a point 44° due north of the sink on the equator. This suggested that the true value should be 45°, and on looking at a sphere this is seen to follow from symmetry although it was not obvious on the map. Thus again we have a confirmation of the passable accuracy of the graphic method—the error here is 1 degree in 90 or 1.1 per cent. of the range.

So far we have only treated the problem as relating to a spherical shell. But we may next suppose the sphere solid and V to be independent of the radius. We will then have a solution of Laplace's equation in space. Since the chequer ratio is constant, the magnitude of the flux is inversely proportional to the linear dimensions of the chequer (on the sphere not on the map) and is consequently proportional to  $\frac{1}{r}$  along any guiding line, r being the radius. But if we draw any small cone enclosing the polar axis—which is now a line source—we see that the outflow between two spheres r and

 $r + \delta r$  is proportional to  $\delta r \times$  (magnitude of flux)  $\times$  (perimeter of the trace of the cone), and by the above this is proportional simply to  $\delta r$ . Therefore the polar axis must be a

Fig. 4.



line source of uniform strength and similarly for any other source or sink when the guiding lines are straights passing through a common point—the strength must be independent of the radius.

Case (b).—General method for conduction in a thin shell of any shape, the thickness and conductivity being any given Phil. Mag. S. 6. Vol. 15. No. 86. Feb. 1908.

functions of position on its surface, and all conditions being constant throughout the thickness of the shell at any point of its surface. Take a solid bounded by a surface of the shape of the shell and draw small rectangles at numerous points of

the surface, so that their chequer ratio =  $\frac{\text{length along flow}}{\text{breadth across flow}}$ 

is directly proportional to the product of the thickness and conductivity at each point of the shell. For then the flow through each chequer will be the same. Suppose that these standard chequers are in some distinctive colour, say red. Now lay off in black the boundary conditions of the special problem and draw a black chequerwork to have the same chequer ratio as the red at each point, much as was done for symmetry about an axis. The standard red chequers need not be connected so as to form two systems of orthogonal lines but may be scattered anyhow over the surface, all that is necessary is that they should be sufficiently small and numerous.

Or it may be convenient to use a projection of the surface as was done in the case of the spherical shell above.

Case (c).—When there exists no family of surfaces normal to the guiding lines. Without pausing for generalities we

will proceed at once to:-

Screw symmetry about an axis.—Let us discuss this with the aid of cylindrical coordinates  $r, \phi, z$ . At a point P on the axis OZ let a perpendicular be drawn extending to infinity. This perpendicular, which is to project only on one side of the axis, is imagined to revolve round the axis and slide along the same with proportional velocities. In one rotation round the axis let it move l along the axis. Then the line sweeps out a surface, at all points of which the expression  $z - \frac{l}{2\pi}\phi$  is constant. Let us put  $z - \frac{l}{2\pi}\phi = \omega$ .

Then as  $\omega$  varies we pass from one of these screw surfaces to another formed by shifting the first parallel to z. The range of the coordinate  $\omega$  is from 0 to l. The intersections of  $\omega$ =const. with the cylinders r=const. are a family of screw-threads.

Let  $d\eta$  be an element of distance measured along any screw guiding line, so that  $\frac{d\eta}{dz} = \frac{\text{length of turn of screw}}{l} = \text{a function of } r \text{ only.}$  And let us make V a linear function of distance along each screw-thread so that  $\frac{\partial V}{\partial \eta} = \text{a function}$  of r only.

Then as  $d\eta$ ,  $d\omega$ , and dr are in perpendicular directions they are independent and

$$\frac{\partial \mathcal{V}}{\partial \mathcal{V}} = \frac{\partial \omega}{\partial \mathcal{V}} \cdot \frac{\partial z}{\partial \omega} + \frac{\partial z}{\partial \mathcal{V}} \cdot \frac{\partial z}{\partial \eta} + \frac{\partial v}{\partial \mathcal{V}} \cdot \frac{\partial z}{\partial z},$$

which reduces to  $\frac{\partial V}{\partial z} = \frac{\partial V}{\partial \omega} + a$  function of r only.

Therefore

$$= \frac{\partial \omega_{s}}{\partial z_{s}} + \frac{\partial z}{\partial u} \cdot \frac{\partial w}{\partial u} \cdot \frac{\partial w}{\partial u}$$
$$= \frac{\partial z}{\partial v} + \frac{\partial z}{\partial u} \cdot \frac{\partial w}{\partial u} - \frac{\partial z}{\partial u} \cdot \frac{\partial w}{\partial u} - \frac{\partial w}{\partial \frac{\partial$$

Again,

$$\frac{\partial \mathbf{V}}{\partial \phi} = \frac{\partial \mathbf{V}}{\partial \omega} \cdot \frac{\partial \omega}{\partial \phi} + \frac{\partial \mathbf{V}}{\partial \eta} \cdot \frac{\partial \eta}{\partial \phi} = \frac{l}{2\pi} \cdot \frac{\partial \mathbf{V}}{\partial \omega} + \text{a function of } r \text{ only.}$$

Since

$$\frac{d\eta}{d\phi} = \frac{\text{length of turn of screw}}{2\pi} = \text{a function of } r \text{ only.}$$

 $\mathbf{A}$ nd so

$$\frac{\partial^{2} V}{\partial \phi^{2}} = \frac{l}{2\pi} \cdot \frac{\partial}{\partial \phi} \left( \frac{\partial V}{\partial \omega} \right) = \frac{l}{2\pi} \left( \frac{\partial \omega}{\partial \phi} \cdot \frac{\partial}{\partial \omega} + \frac{\partial \eta}{\partial \phi} \cdot \frac{\partial}{\partial \eta} \right) \frac{\partial V}{\partial \omega}$$

$$= + \frac{l^{2}}{4\pi^{2}} \cdot \frac{\partial^{2} V}{\partial \omega^{2}}.$$

Now substitute these values of  $\frac{\partial^2 V}{\partial z^2}$  and  $\frac{\partial^2 V}{\partial \phi^2}$  in the expression for  $\nabla^2 V$  in cylindrical coordinates, and we have

$$\nabla^2 \mathbf{V} = \frac{\partial^2 \mathbf{V}}{\partial r^2} + \frac{1}{r} \frac{\partial \mathbf{V}}{\partial r} + \left(1 + \frac{l^2}{4\pi^2 r^2}\right) \frac{\partial^2 \mathbf{V}}{\partial \omega^2},$$

which contains only two coordinates r and  $\omega$ . So that if we make  $\nabla^2 V = f(V, r, \omega)$  over any surface the same will be true throughout the whole region filled by the screw-threads

passing through the surface, provided that  $\frac{\partial V}{\partial \eta}$  is such as to make  $\frac{\partial^2 V}{\partial r^2} + \frac{1}{r} \frac{\partial V}{\partial r}$  constant along every guiding screw. One way of satisfying this is to make V increase by the same

One way of satisfying this is to make V increase by the same amount per turn of the screw, along every screw-thread and so that  $\frac{\partial^2 V}{\partial r^2}$  and  $\frac{\partial V}{\partial r}$  are both constant along every guiding

screw.

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In the following pages, except where specially indicated, we will consider only the case  $\frac{\partial V}{\partial \eta} = 0$ .

As this result does not appear to be given in the text-books, it may be well to confirm it by a slightly different line of reasoning, as follows. The tangent of the angle between the tangent to any screw-threads and a plane normal to the axis of symmetry is  $\frac{l}{2\pi r}$ .

Therefore the first space rate of any function of position V along the tangent to a screw-thread is

$$\frac{1}{\sqrt{l^2+4\pi^2r^2}}\left\{2\pi r\frac{\eth}{r\eth\dot{\phi}}+l\frac{\eth}{\eth z}\right\}V.$$

If  $\frac{\partial V}{\partial \eta}$  = a function of r only, along every screw-thread then we have a function of r only  $+2\pi\frac{\partial V}{\partial \phi} = -l\frac{\partial V}{\partial z}$  throughout the whole region. Therefore this last equation will still remain true after differentiation by  $\phi$  or by z, thus

$$-\frac{2\pi}{l}\frac{\partial^{2}V}{\partial\phi^{2}} = \frac{\partial^{2}V}{\partial\phi\partial z},$$
$$\frac{\partial^{2}V}{\partial\phi\partial z} = -\frac{l}{2\pi}\frac{\partial^{2}V}{\partial z^{2}}.$$

Equating the two values of  $\frac{\partial^2 V}{\partial \phi \partial z}$  thus obtained we have

$$\frac{\partial^2 V}{\partial \phi^2} = \frac{l^2}{4\pi^2} \frac{\partial^2 V}{\partial z^2},$$

which on substitution in the expression for ∇2V gives

$$\nabla^2 \mathbf{V} = \frac{\partial^2 \mathbf{V}}{\partial r^2} + \frac{1}{r} \frac{\partial \mathbf{V}}{\partial r} + \left(1 + \frac{l^2}{4\pi^2 r^2}\right) \frac{\partial^2 \mathbf{V}}{\partial z^2}.$$

But it is now to be observed that if the distribution of V on any plane passing through the axis of symmetry is known, then V is determined everywhere. And on such a fixed plane the contours of z are identical with those of  $\omega$ . So that we may replace z by  $\omega$  in the last equation, and the previous result is confirmed.

We have shown that if we make  $\nabla^2 \mathbf{V} = f(\mathbf{V}, r, \boldsymbol{\omega})$  over any surface intersecting all the screw-threads, the same will

be true throughout the whole region, with the stated provisions as to the value of  $\frac{\partial V}{\partial \eta}$ . The geometrical meaning of

this result is that if we draw any infinitesimal rectangle normal to one of the screw-threads and draw screw-threads through each of its four corners, then the infinitesimal tube thus formed will be everywhere rectangular in normal cross section, and more than this, the rectangle will have the same ratio of length to breadth and will be of the same size at all points along the tube. For if we consider one pair of opposite faces of the tube as equipotentials and the other pair as lines of flow, then these properties are seen to follow from the fact that  $\nabla^2 V$  is constant along a screw-thread when V is constant along the same. And indeed these properties are immediately obvious from the appearance of the system.

Consequently, if we take any family of surfaces  $\alpha$  passing through the guiding screw-threads, there will always be an orthogonal family of surfaces  $\beta$ , also passing through the screw-threads. If the surfaces  $\alpha$  are the contours drawn at equal intervals of the potential V the surfaces  $\beta$  are stream-

surfaces. And  $\frac{H_{\alpha}}{H_{\beta}}$  may be named the "Chequer Ratio" consistently with what has gone before. If  $\nabla^2 \alpha$  is to vanish we must have

$$\frac{\partial}{\partial\alpha}\left(\frac{H_{\alpha}}{H_{\beta}\times \frac{\text{(length of portions of successive screw-threads intercepted}}{\text{between two stream-lines lying on the same stream-surface}}\right)=0.$$

Since the screw system is uniform the length of the portions of successive screw-threads intercepted between two stream-lines lying on the same surface  $\beta$  can be proportional to nothing else than the length of one turn of the screw-thread at the radius considered. For the two stream-lines in question must by symmetry make equal angles with planes normal to the axis of the screw, at each pair of points lying on the same screw-thread. So that the projection of the distance between the said pair of points onto the axis of the screw will be always the same fraction of l as the points move from one screw-thread to another.

Now the length of an arc ds of a screw-thread being

$$\sqrt{dz^2 + r^2} d\theta^2 = d\theta \sqrt{\frac{l^2}{4\pi^2} + r^2},$$

258 Mr. L. F. Richardson on a Freehand Graphic way the length of one turn is

$$\int_{0}^{\theta=2\pi} ds = 2\pi \sqrt{\frac{l^2}{4\pi^2} + r^2} = l\sqrt{1 + \frac{4\pi^2 r^2}{l^2}}.$$

Therefore we may satisfy the equation  $\nabla^2 \alpha = 0$  by making  $\frac{H_{\alpha}}{H_{\beta}}$  proportional to  $\sqrt{1 + \frac{4\pi^2 r^2}{l^2}}$  as the radius varies. A table giving the values of  $\sqrt{1 + \frac{4\pi^2 r^2}{l^2}}$  for a number of values of  $\frac{r}{l}$  is annexed.

$\frac{r}{l}$ .	$\sqrt{1+\frac{4\pi^2r^2}{\ell^2}}$	For standard chart.		$\frac{l}{2\pi r}$
	l times this equals are of one turn of thread.	H <sub>a</sub> .	$\mathbf{H}_{\boldsymbol{\beta}}.$	equals tangent of angle between helix and circle.
0	1.0000	•5507	1.8157	<b>o</b> o
05	1.0482	.5639	1.7735	3·1831
10	1.1811	.5985	1.6707	1.5916
15	1.3741	.6456	1.5490	1.0610
•20	1.6060	6979	1.4328	•7958
·30	2.1338	·8045	1.2430	.53052
•40	2.7049	.9058	1.1040	39789
.50	3.2969	1.0000	1.0000	31831
.60	3.9003	1.0877	.9194	•26526
.70	4.5105	1.1697	.8550	22736
-80	5.1251	1.2468	.8021	19894
.90	5.7426	1.3198	.7577	17684
1.00	6.3623	1.3892	.7199	·15916
1.5	9:478	1.6955	•5898	•10610
2.0	12.606	1.9554	.5114	.07958
2.5	15.740	2.1850	.4577	06366
3.0	18.876	2.3928	4179	05305
3.5	22.014	2.5840	3870	.04547
00	, ∞	00	0	00

It is hoped that these values are correct to less than half a unit in the last place.

As there is no surface normal to the screw-threads, it is not possible to draw standard rectangles of the appropriate chequer ratio for each distance from the axis. But as the whole distribution of V is determined when the section of it by a plane passing through the axis of the screw is known,

we may draw on this plane the sections of tubes formed by the surfaces  $\alpha$  and  $\beta$  in such a way that  $\frac{H_{\alpha}}{H_{\beta}}$  is proportional to

$$\sqrt{1+rac{4\pi^2r^2}{l^2}}.$$

The sections of these tubes will in general not be rectangles: in fact, the angles and ratio of sides of the chequers formed by the traces of  $\alpha$  and  $\beta$  on the plane  $\phi = \text{constant}$  will both now depend on the orientation of the chequer as well as on its distance from the axis. It will therefore be necessary to make a chart of standard chequers in various orientations at a number of distances from the axis. Plate XII, is such The rectangles in the right-hand margin represent normal cross sections of the tubes formed by the surfaces  $\alpha$  and  $\beta$ . In a line with each of these are five sections of a tube of the same size and shape by the plane of the paper, when the angle between one face of the tube and the normal to the axis of the screw is successively  $0^{\circ}$ ,  $22\frac{1}{2}^{\circ}$ ,  $45^{\circ}$ ,  $67\frac{1}{2}^{\circ}$ , 90°. In order to be clearly visible these parallelograms are drawn quite large. What each really represents is the shape of an infinitesimal chequer situated at the central point of the large one. Practically the difference will not be important.

Now this standard diagram can be covered by a sheet of tracing-paper, and two intersecting families of lines drawn on the tracing-paper in such a way that the parallelograms formed by them are everywhere similar to the chequers underneath, which have the same distance from the axis and the same orientation on the paper. Then if this tracing-paper plane rotate round the axis and slide along it so as to follow the guiding lines, the equipotential lines on the paper will sweep out the contours at equal intervals of V in space in such a way that  $\nabla^2 V = 0$  and the other family of lines will

sweep out stream-surfaces. A quantity which it is frequently necessary to determine

is the magnitude of the flux

Since 
$$= \sqrt{\left(\frac{\partial V}{\partial x}\right)^2 + \left(\frac{\partial V}{\partial y}\right)^2 + \left(\frac{\partial V}{\partial z}\right)^2} = \frac{1}{H_a}.$$

$$\frac{H_a}{H_B} = A\sqrt{1 + \frac{4\pi^2 r^2}{l^2}},$$

Since

260 Mr. L. F. Richardson on a Freehand Graphic way where A is an absolute constant, we must have

$$\frac{1}{\mathbf{H}_a} = \mathbf{A} \frac{\sqrt{1 + \frac{4\pi^2 r^2}{l^2}}}{\mathbf{H}_{\beta}}$$

So that  $\beta$  is a stream function analogous to the forms in use when the guiding lines are parallel straights or circles with their centres on, and their planes normal to, a common axis.

In types previously studied, when the graph was drawn on a surface normal to the guiding lines,  $H_a$  and  $H_{\beta}$  were proportional to the length and breadth of a chequer and could be measured directly. But here we must first compare the linear dimensions of a freehand chequer with those of the standard oblique section of the tube bounded by two stream-surfaces and two equipotentials, and then refer to the normal section of the same tube in the right-hand margin of the chart.

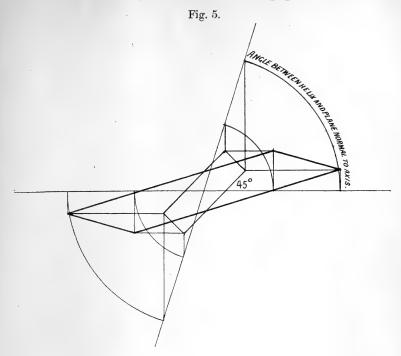
The standard chequers were obtained in the following

 $\frac{H_{\alpha}}{H_{\beta}}$  being equal to constant  $\times \sqrt{1 + \frac{4\pi^2 r^2}{l^2}}$ , some other relation is necessary to determine  $H_{\alpha}$  and  $H_{\beta}$  separately. The relation  $H_{\alpha} \times H_{\beta} = 1$  was chosen for this purpose, as this gives a neat appearance to the standard chart. It was also found convenient to make the constant such that  $\frac{H_{\beta}}{H_{\alpha}} = 1$  when  $\frac{r}{l} = 0.5$ . The values of  $H_{\alpha}$  and  $H_{\beta}$  were calculated and are given in the accompanying table. The sides of the

and are given in the accompanying table. The sides of the rectangles in the right-hand margin of the standard chart were drawn proportional to  $2H_a$  and  $2H_g$ .

To obtain the slant section, the tangent of the angle between the tangent a guiding-line and the plane normal to the axis of the screw, was first calculated. It is equal to  $\frac{l}{2\pi r}$ , and is given in the table under that head. The rectangles were then projected with ruler and compasses in a manner which is perhaps sufficiently indicated by fig. 5,

which shows the construction when  $\frac{r}{l} = 0.05$  and the angle between a radius from the axis of symmetry and the tangent plane to the surface  $\alpha = \text{constant}$  meeting at the point considered is 45°.

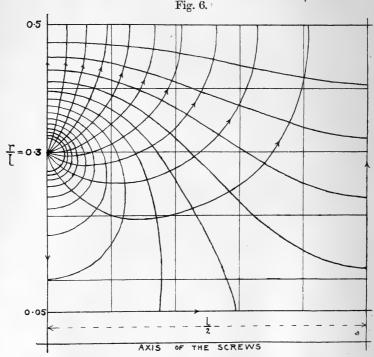


Of the innumerable solutions of  $\nabla^2 V = 0$  possessing screw symmetry of the sort described, which may be obtained by the aid of this standard chart, perhaps the simplest is the field due to a helical line source, such for example as the distribution of temperature in a mass of electrically insulating material which encloses a helical copper wire carrying an electric current. To avoid the introduction of a difficulty not characteristic of screw symmetry, I have assumed a core of non-conducting material in the form of a circular cylinder surrounding the axis. This relieves us of the necessity of considering the axial line of equilibrium, which would otherwise have to be treated by an extension of the method in The external surface of the medium is also taken as a circular cylinder and is assumed to be at constant Consistently with our boundary conditions temperature.

we may suppose that  $\frac{d\mathbf{V}}{d\eta} = 0$ . Now symmetry will help us in several ways, for since the chequer ratio on the standard chart is the same whether any particular half-turn of the screw passes over or under the chart, one sees on beginning

to make the drawing, that the two surfaces  $\omega = \text{const.}$ , which pass respectively through the electric current and half-way between two adjacent turns of the current, must be surfaces of flow. Again, very close to the electric current the flow of heat will be nearly the same as that due to a straight current tangential to the helix, that is to say, the lines of flow will be normals to the helix and the isothermals will approximate to circular cylinders concentric about the tangent.

The particular dimensions chosen were  $\frac{r}{l}$ =0.05 for the core, 0.3 for the source, and 0.5 for the outer cylinder.



Owing to orientation of the chequer affecting its shape this graph took twice or thrice as long to adjust as did the others in this paper. Its errors are discussed in Section VIII. hereafter.

The magnetic field due to the helical current may doubtless be determined in a very similar manner. Here  $\frac{\partial V}{\partial \eta}$  will be a constant other than zero and the cyclical properties of the field will add a further complication.

We have hitherto passed over without mention the peculiarities relating to points of equilibrium—these are points at which the first space-rate of the potential vanishes in all directions. In the neighbourhood of these the chequers become unusually large, and if any chequer goes right up to an equilibrium point it will not have the shape characteristic of its neighbours, but will take a peculiar form of its own.

There are several diagrams of this in Maxwell's 'Electricity

and Magnetism.' See, for example, vol. ii. fig. xvii.

Now if V be expressed in terms of rectangular coordinates u and v lying in the plane of the graph with their origin at the equilibrium point, then linear terms in V must vanish, and we have

$$V = Au^2 + B\omega + Co^2 + Eu^3 + Fu^2v + Guv^2 + \text{ terms of higher degree.}$$

Now let us make  $\nabla^2 V$  vanish.

For guiding lines parallel straight and normal to the plane of the graph

$$\nabla^2 V = \frac{\partial^2 V}{\partial u^2} + \frac{\partial^2 V}{\partial v^2} = 2(A + C) + u(6E + 2G) + v(2F + 6H).$$

When the graph is on a plane passing through an axis about which there is symmetry of revolution and u is normal to this axis, we must add to the above value of  $\nabla^2 V$  the term

$$\frac{1}{r}\frac{\partial \mathbf{V}}{\partial u} = 2\frac{u}{r}\mathbf{A} + \frac{v}{r}\mathbf{B} + 3\frac{u^2}{r}\mathbf{E},$$

where r is distance from the axis.

Now when the point considered is not on or close to the axis, it will be possible to put in so many chequers that the first two chequers in any direction from the equilibrium point require for their measurement so small a range of u

and v that the fractions  $\frac{u}{r}$ ,  $\frac{v}{r}$ , &c., will be small, and therefore

the additional terms which come in for symmetry about an axis may be neglected, and we have the same form for  $\nabla^2 V$  in both cases.

Further, since Mercator's projection does not alter the shape of any small pieces,  $\nabla^2 V$  will have the same form in the neighbourhood of an equilibrium point on the Mercator's plan of the distribution on a sphere.

This being so, the general form of V in all three cases is

 $V = a(u^2 - v^2) + b \cdot uv + g(u^3 - 3uv^2) + h(v^3 - 3u^2v) + higher terms,$ 

where a, b, g, and h are arbitrary constants. When the ratios of a and b to the succeeding coefficients do not vanish, then the first two terms are all that we need consider. Now it may easily be shown that by a proper rotation of the axes of reference, so that uv transform to  $u_1v_1$ , the sum of these two terms may be transformed into either of them separately. We need therefore only consider one, say  $bu_1v_1$ . The contours of this function are hyperbolas and are orthogonal to

those of  $a(u_1^2-v_1^2)$ . The ratio  $\frac{a}{b}$  is determined by the chequer

ratio in the neighbourhood of the equilibrium point.

A graph of this function for the special case of unit chequer ratio is given in Webster's 'Dynamics,' p. 525, and shows that two equipotentials meet at right angles at the equilibrium point, and that two stream-lines also pass through the same point and bisect the angles between the equipotentials. The eight curved chequers which meet in the point each have consequently three corners of 90° and one of 45°. A graph of this function may be used as a "standard equilibrium point" to keep the eye informed of the necessary proportions of the first and second ring of chequers surrounding the point.

If, however, the coefficients a and b vanish, while g and h do not, then the terms of the 3rd degree become all

important.

By rotating the axes the sum of the two terms of the 3rd degree may be reduced to either separately. A rough graph of the contours of these functions is given by Fiske in Merriman & Woodward's 'Higher Mathematics,' p. 248. Here three equipotentials intersect in the equilibrium point. And three stream-lines bisect the angles of 60° which are formed in this way.

Now when a graph has to be drawn and is found to contain an equilibrium point, the general arrangement of the potential will give us the clue as to whether two, three, or more equipotentials intersect in the equilibrium point. And this being known, we have only to draw in the standard type at the

proper dimensions and chequer ratio.

When the graph is drawn on a plane passing through an axis about which there is screw symmetry of the sort described in Section III c, then the appearance is different, for we have to add to the value of  $\nabla^2 V$  for circular symmetry about

an axis the term

$$\frac{l^2}{4\pi^2r^2} \cdot \frac{\partial^2 V}{\partial v^2} = \frac{l^2}{4\pi^2r^2} (2C + 2uG + 6vH).$$

And therefore writing

$$1 + \frac{l^2}{4\pi^2 r^2} = \mathbf{R}^2$$

we have

$$\mathbf{V} = a(\mathbf{R}^2 u^2 - v^2) + b \cdot uv + g(\mathbf{R}^2 u^3 - 3uv^2) + h(v^3 - 3\mathbf{R}^2 u^2 v).$$

A simpler way of looking at the matter is to consider a tiny plane element normal to the guiding screw which forms the line of equilibrium. The normals to the surfaces  $\omega = \text{const.}$  lie in this plane. If  $dS_{\omega}$  distance along such a normal, then

$$d\boldsymbol{\omega} = dS_{\boldsymbol{\omega}} \sqrt{\left(\frac{\partial \boldsymbol{\omega}}{\partial z}\right)^2 + \left(\frac{1}{r}\frac{\partial \boldsymbol{\omega}}{\partial \phi}\right)^2} = dS_{\boldsymbol{\omega}} \sqrt{1 + \frac{l^2}{4\pi^2 r^2}}.$$

Substituting this in the expression of  $\nabla^2 V$  in terms of r and  $\omega$  we have

$$\nabla^2 \mathbf{V} = \frac{\partial^2 \mathbf{V}}{\partial r^2} + \frac{1}{r} \frac{\partial \mathbf{V}}{\partial r} + \frac{\partial^2 \mathbf{V}}{\partial \mathbf{S}_{\omega}^2},$$

just as if  $S_{\omega}$  was z in circular symmetry about an axis. From this we see that the appearance of the equilibrium point on a small plane element normal to the guiding screw will be exactly similar to the forms already dealt with. Its appearance on a plane which passes through the axis of the screw may be sketched without much difficulty by comparing the chequers in the right-hand margin of the standard chart with their projections as drawn in the middle of the chart.

## V. Equations other than Laplace's.

It has been shown above that in order to solve the equation

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} = \text{any given function of V, } x, y,$$

a relation between differences of chequer ratios has to be satisfied. And the same will be found to be true for the other forms of the equation  $\nabla^2 V = a$  function (of V and of position) which can be treated by two coordinates. A difference relation of the sort referred to would involve the comparison of each chequer with a standard set having graded chequer ratios, followed by the calculation of  $\nabla^2 V$  by

arithmetic. And although it would doubtless be possible to carry out the necessary operations, yet it would almost certainly be quicker and more accurate to use-arithmetical finite differences altogether, writing in the numerical values of V at a set of points on the paper and adjusting these numbers until the finite difference equation is satisfied,—in a manner which may be described in a future paper. In view of this I will not attempt to elaborate freehand methods for  $\nabla^2 V =$  a given function of V and of position.

There are, however, certain common space distributions which may be treated graphically with simplicity although

they do not satisfy  $\nabla^2 V = 0$ .

Firstly, when the conductivity is a continuous function of position, and the direction of the flux is normal to the contours of a potential, and the magnitude of the flux is the maximum space-rate of the potential multiplied by the conductivity, and the flux has no divergence. For example: the flow of heat and electricity in isotropic but non-homogeneous bodies, or the soakage of water in a saturated subsoil the upper layers of which are more porous than those below. Let K be the conductivity and suppose that it is constant along each guiding line but varies from one such line to another. Then, when the lines have a family of surfaces normal to them we must have

$$\frac{\partial}{\partial \alpha} \left( \frac{H_{\beta} \cdot H_{\gamma} \cdot K}{H_{\alpha}} \right) = 0$$

in order that the flux shall not diverge. This is very easily assured by preparing the paper with standard chequers

having their chequer ratio  $\frac{H_a}{H_s}$  proportional to  $H_\gamma$ . K. In

fact, we have an example of this in Section III a above; for circular symmetry about an axis may be regarded for this purpose as flow between parallel planes in a medium having conductivity directly proportional to the distance from the axis. And reciprocally.

Similarly in the case of screw symmetry, standard chequers

are to be prepared having

$$\frac{H_{\alpha}}{H_{\beta}}$$
 proportional to  $K\sqrt{1+\frac{4\pi^2r^2}{l^2}}$ .

Two other cases can probably be treated freehand, namely, the flow of heat in bodies where the conductivity varies with the temperature, and, of great practical importance, the distribution of magnetic induction in soft iron, taking into account the variation of the permeability with the force. But these again will be left to those who need the results.

# VI. Note on Boundary Conditions.

It may be convenient to the reader if we bring together certain well-known facts concerning boundary conditions.

Let us regard V simply as a function of position, not necessarily satisfying  $\nabla^2 V = 0$  or any other equation; and, as always, let contours be drawn at small intervals of V each equal to k. Then the first space-rate of V in any direction at a point is inversely as the intercept cut off from a line in that direction by two contours of V one on each side of the point, and is directly as K. Suppose, further, that the whole distribution of V can be represented by a single graph.

1. If we have to make V such that the magnitude and direction of its maximum first space-rate, the Hamiltonian vector  $\nabla V$ , satisfies given values over a boundary of a given shape. Then it is easy to set off the ends of the contours of V with a ruler and scale, for their directions are known and

also the distance apart of successive pairs.

2. If we are not given  $\nabla V$  over the boundary but only the first space-rate of V in a given direction. Then there are an indefinite number of ways in which the contours of V may cut the boundary; and as it will not generally be possible to say which of these is consistent with the internal conditions, they must be drawn and modified freehand as the approximation to the internal conditions proceeds. This is usually not difficult.

3. To make V continuous at any surface cutting the distribution, all that is necessary is that the ends of the contours of V approaching from the two sides should meet one another at this surface. Whether they meet at an angle or not does not matter.

4. To make the first space-rates of V in every direction continuous at any surface where V is continuous, not only must the contours of V meet one another, but they must pass smoothly into one another without making an angle. For if they made an angle and a straight line were drawn tangent to one branch of the contours at the angle, then the ratio of successive intercepts of this line by the contours of V would not become unity when the contours were drawn at indefinitely small intervals of V, so that the second space-rate along this straight would be indefinite at the angle.

5. Suppose next that a non-divergent vector is normal to

the surfaces V=const., and that the magnitude of the vector is equal to the space-rate of V along the said normal, multiplied by a scalar function of position; which according to the particular application will be the conductivity, permeability or some other specific constant. Then we may require the conditions which must hold at a boundary where the specific constant has a discontinuity while V is continuous—as, for example, where magnetic flux passes from air into mild steel. These conditions, which I take from Prof. J. J. Thomson's 'Elements of Electricity and Magnetism,' may be stated thus:—If  $K_1$ ,  $K_2$  are the aforesaid specific constants on the two sides of the boundary, and  $\theta_1$  and  $\theta_2$  are the corresponding angles which the direction of the vector makes with the bounding surface, then

$$\frac{1}{K_1}\tan\theta_1 = \frac{1}{K_2}\tan\theta_2.$$

Now if the graph be drawn on a surface which is normal to the guiding lines, the direction of the vector lies in the graph, and  $\theta_1$  and  $\theta_2$  are the actual angles which one sees. The same is true of the Mercator's map of a spherical surface distribution, since the angles are unchanged by projection. But with our method for screw symmetry, the angles  $\theta_1$  and  $\theta_2$  do not immediately appear, and comparison must be made with the angles of the slant sections of the rectangular tubes given on the standard chart.

# VII. Miscellaneous Notes on Draughtsmanship.

(a) Since with the exception of given boundaries and lines deduced from symmetry no part of the field can be said to be correct until the whole field is correct, it is advisable to begin by covering the whole field with intersecting lines, however erroneous they may be, and then to carry out amendments over wide areas at one time.

(b) In the final stages of a drawing intended improvements often overshoot the mark or cause unforeseen disturbances in the surrounding chequers. It seems well, therefore, to lay aside the indiarubber after a certain accuracy has been reached, and, placing a sheet of tracing-paper over the rough diagram, to draw the intended improvements upon this. And so with all later stages. The tracing-paper diagrams are then compared with one another and the best selected.

(c) The graphic addition of two scalar functions of position is conveniently performed in the way described by Maxwell ('Elementary Treatise on Electricity') by laying the contours drawn on a sheet of tracing-paper at equal intervals of the one over those of the other, covering the two with a clean

sheet of tracing-paper, and drawing the diagonals of the chequers formed by the intersecting contours.

### VIII. Estimation of Errors.

To one reading an account of this freehand method without having worked an example, it might seem as if there were no way of setting a limit to the errors of any particular graph. This, if it were true, would be a serious fault. But, happily, it is not so; for it is commonly necessary to make several drawings and then select the best of them: so that by the time the draughtsman has reached a drawing which he can scarcely improve upon, he has before him deviations from it in divers directions. The difference, then, between the selected graph and the second best graphs is a measure of the errors of the latter and an outside limit to the errors of the former. The actual errors of the selected graph will be less than this limit, and may be estimated by comparing the errors in the shape of the individual chequers in the best and second best graphs, and taking a fraction, thus:—

individual chequer error in best graph same in second best graph (difference between best and) •

This is the true measure of the errors of the best graph. It depends, of course, on a general mental estimate or appreciation, and is consequently not susceptible of exact definition. But this does not much matter, for if the value of an error be known within two times either way it is usually sufficient.

The difference between the best and second best graphs is less dependent on a mental estimate, and consequently sets a

firmer limit to the possible error.

Taking, for example, the graph of the field round a helical line source given in section III. c, and laying over it the tracing of the unpublished second-best graph, one sees that the difference in position of the lines in the two graphs nowhere exceeds ½ the linear dimension of the chequer, at the point and in the direction considered. Now I should estimate that the error of the shape of individual chequers in the published graph averaged \frac{1}{2} of the same quantity in the other: so that \(\frac{1}{4}\) of the linear dimensions of the chequer may be taken as the error of position of the lines in the published graph. Now the graph exhibits ten tubes of flow; so that 1/4 of one tube is  $2\frac{1}{2}$  per cent of the range. This is in the worst parts of the field. Elsewhere the error will be less, but it may still be expected to exceed the errors found when the graph is drawn on a surface normal to the guiding lines, because in the case of screw symmetry we have the added difficulty that the shape of the chequers depend upon its orientation.

XXII. Anomalous Magnetic Rotatory Dispersion of Neodymium. By R. W. Wood, Professor of Experimental Physics in the Johns Hopkins University\*.

#### [Plate XIII.]

THERE has been a good deal of discussion as to whether anomalous dispersion of the rotatory polarization occurs in the vicinity of the absorption-bands of the rare earths. The work of Bates, as well as my own, appears to have proven beyond much question that the aniline dyes do not exhibit the phenomenon, as was claimed by Schmauss, who published curves which apparently showed very pronounced anomalies at the absorption-bands. Schmauss also investigated the magnetic rotation of solutions of the rare earths (Annalen der Physik, x. p. 853, 1903), and found that there was, in every case, an abnormal increase of the rotation on the red side of the bands, and an abnormal decrease on the blue side, as in the case of ordinary anomalous dispersion. Bates was unable to find any anomalies whatever, but an examination which I made of a solution of praseodymium appeared to confirm, at least in a measure, the results of Schmauss (Phil. Mag. May 1905; Phys. Zeit. vi. p. 416, 1905).

As I stated in my earlier paper, it was difficult to get results in which one could feel absolute confidence, owing to the great experimental difficulties. I had no polarimeter of precision, and was obliged to work with a pair of nicols only, and determine the rotation of the plane by the method of extinction.

If one could deal with rotations of sufficient magnitude to enable one to obtain a dark band in the spectrum of the transmitted light, one could feel sure of the results, and this I have at last succeeded in doing. To my great surprise, however, in the case of the one band which has been carefully studied, the anomaly is the same as with sodium vapour, that is the rotation increases very rapidly as the absorption-band is approached from the short wave-length side. It has been found possible to set the nicols for extinction and cause a restoration of the light in the vicinity of the absorption-band by the excitation of the magnet, as can be so beautifully done with the non-luminous vapour of metallic sodium †. This is proof positive that the phenomenon exists, and I have even

\* Communicated by the Author.

<sup>†</sup> Macaluso and Corbino, Rend. Real. Ac. dei Lincei (5) vii. p. 293. Wood, "Magnetic Rotation of Sodium Vapour," Phil. Mag. Oct. 1905; and July 1907.

succeeded in photographing the spectrum of the restored

light.

The neodymium nitrate was prepared in the form of a solid film, amorphous and isotropic, pressed between two very thin cover-glasses. The nitrate was prepared from the double ammonium salt by precipitation with oxalic acid, ignition, and treatment with nitric acid. The nitrate, freed from acid, was boiled down to the consistency of syrup, in which state a drop placed on a strip of glass will immediately solidify into a clear glass bead without crystallization, a fact found by Anderson in the course of his investigations upon the absorption spectra of the rare earths. By forming a prism of about 40 degrees of this substance between plates of heated glass, I have detected anomalous dispersion at the absorption-band at wave-length 5790, something which I have never been able to do with solutions, even with compensated prisms.

The films are not at all difficult to prepare. The coverglasses are heated and a small drop of the molten substance pressed out between them. If crystallization occurs, it indicates that the solution has not been sufficiently boiled down. Films varying in thickness from 0.1 to 0.5 mm. were used, the best results being obtained with a moderate thickness.

The light from an arc-lamp was passed through a nicol and the cores of a large Ruhmkorff magnet, between the poles of which the film was mounted, then through a second nicol, after which it was concentrated on the slit of a spectro-The nicols were set for extinction, which could be done to within a tenth of a degree, after which the magnet was excited. A restoration of the light immediately occurred throughout the whole range of the spectrum in the case of the thickest films, the intensity being greatest however in the vicinity of the absorption-band. With thinner films the restoration was confined to the immediate vicinity of the band, a bright and very narrow line shining out exactly in coincidence with the centre of the absorption-band, with fainter bands on each side (Pl. XIII. fig. 1). The direction of the rotation was the opposite of that produced by a plate of glass placed between the poles of the magnet, and was about four times as great. It immediately occurred to me that what we may term the rotation of the substance as a whole (that is the rotation due to infra-red and ultra-violet electrons) could be practically compensated by employing glass plates of the requisite thickness, leaving an outstanding effect due solely to the absorption-bands which fell within the limits of the visible spectrum; and this method was successfully

employed in some of the work, though there does not appear

to be any especial benefit derived from its nse.

As is well known, when the nicols are set for extinction, and the light is restored in the spectroscope by the excitation of the magnet, a dark band enters the red end of the spectrum and moves towards the violet, when the analysing nicol is turned in the direction in which the rotation of the plane of polarization has occurred. This means of course that the rotation increases as the wave-length decreases. In the case of the neodymium film, the reverse was found to be true, the band moving up from the blue towards the yellow, until it was driven into the absorption-band and lost, indicating that the rotation is abnormally great on the short wave-length side of the band, as is the case with the vapour of sodium. No very marked effect could be detected on the red side.

We will now examine in detail some of the effects which

are seen with films of varying thickness.

The phenomena which are to be discussed occur at the absorption-band at wave-length 5790, and as the appearance of the band is a little different from that exhibited by solutions of the salt it seemed best to photograph it. A film was pressed between two plates of glass in the form of a very acute prism, which when placed in front of the spectrograph slit, and illuminated with white light, gave a photograph which showed the actual form of the absorption curve. The absorption-band is seen to be double, a strong one with its centre at 5790, and a fainter one close to it and on the blue side (fig. 1). A barium-iron are was impressed on the same plate as a comparison spectrum.

When a very thin film is placed between the poles of the magnet and the current turned on, the restoration of the light is only noticeable in the immediate vicinity of the absorption-band. A bright and rather narrow band (about 12 A.E. in width) appears exactly at the centre of the absorption-band, that is at wave-length 5790. On the blue side of this there appears a fainter and broader band midway between the two absorption-bands, while still further along there is another narrow band, in coincidence with the fainter

of the two absorption-bands.

A photograph of this "magnetic spectrum" was made. but it is on too small a scale to reproduce well, and I have accordingly made an accurate drawing from it on the same scale as the absorption spectrum. The state of polarization in this magnetic spectrum appears to be most peculiar. If the analysing nicol is turned a degree or two in the direction in which the rotation has occurred, the bright band at wave-

length 5790 moves distinctly towards the blue, while rotating the nicol in the opposite direction causes a motion towards the red.

If we attempt to explain this behaviour of the band by assuming a certain distribution of plane-polarized light in it, we find that we have a discontinuity in the position of the plane of polarization at the centre of the band. It appears to me that the more probable state of things is as indicated in fig. 2, the polarization at the centre of the band being circular, passing to the state of plane polarization (oppositely inclined) on each side of the band through intermediate ellipses. This means of course that the two circular components of the plane vibration, which by their unequal velocity in the magnetized medium give rise to the rotation of the plane of polarization, are unequally absorbed, a phenomenon which has been observed by Cotton in the case of naturally active bodies.

From a very careful study of the spectrum and the direction of the shift of the dark and light regions in it, I am inclined to regard the rotations as indicated in fig. 2, the

incident vibrations being vertical.

With a thicker film very strong anomalous rotation can be observed in the green. After the restoration of the light by the magnetic field, if the analysing nicol be turned in the direction in which the plane of polarization has been rotated, a broad dark band moves from the blue-green region towards the absorption-band in the yellow, becoming narrower as it moves along, until at the moment when it is at the edge of the absorption-band it is so narrow as to be barely visible. This indicates of course that the curve of the magnetic rotation becomes very steep as we approach the absorption-band from the blue side, precisely as in the case of sodium vapour (fig. 3). On the other side of the absorption-band I am The rotation is unable to determine how the curve runs. apparently about the same as in the blue-green region, and of the same sign, but no certain trace of any moving band could be discerned as the nicol was rotated. The curve is evidently not as steep on the red side, or the band of extinction could certainly be detected in the neighbourhood of the absorption-band. So far as could be determined, rotation of the nicol extinguished the red and orange portions of the spectrum simultaneously, the faint suggestion of a dark band coming in from the red side being in all probability an illusion, for as is well known extinction appears to begin at the faintly visible end of a spectrum, even when it is extinguished uniformly.

We must remember that we are observing rotations which result from a pair of absorption-bands, which may behave in different ways, that is they may conspire for wave-lengths on the blue side and oppose each other for the longer waves on the red side. If, for example, the stronger band at wavelength 5790 gave positive rotations for the red waves, and negative rotations for the green, and the fainter band gave negative rotations for both red and green, the absence of a sharply marked extinction-band on the red side is at once explained. Both types of rotation curves are theoretically possible according to Drude, according to the fundamental hypothesis adopted. The second type is characteristic of sodium vapour, as is well known.

I am now preparing a set of these films for Dr. Bates, of the Bureau of Standards, who plans to investigate them with

a large and very accurate polarimeter.

XXIII. On the Existence of Positive Electrons in the Sodium Atom. By R. W. Wood, Professor of Experimental Physics in the Johns Hopkins University\*.

#### [Plate XIV.]

THE greater part of the evidence which we have obtained thus far regarding the structure of the atom, indicates that the centres of vibration which emit the spectral lines are negatively charged corpuscles. The positive charges appear to be associated with the atom as a whole, and the assumption is often made that the positive electrification is of uniform distribution.

The Zeeman effect shows us that the D lines of sodium are due to vibrators carrying negative charges, a fact which is true of all other lines which show the effect. That a negative charge is associated with the centres of vibration which emit the D lines is also shown by the direction (positive) of the magnetic rotation of the plane of polarization, for waves of very nearly the same frequency as that of the D lines. As is well known band spectra do not show the Zeeman effect at all, consequently we are unable to apply this test to the investigation of the nature of the charge associated with the centres of emission of the lines of which the bands are made up.

Some of the lines which make up the complicated channelled

<sup>\*</sup> Communicated by the Author.

absorption spectrum of sodium vapour, have, as I have shown in previous papers (Phil. Mag. Oct. 1905, Nov. 1906), the power of rotating the plane of polarization when the light is passed through the magnetized vapour in the direction of the lines of force.

White light is passed through a nicol prism and a steel tube which passes through the pole-pieces of a large electromagnet. An analysing nicol, condensing-lens, and spectroscope follow in succession. The tube contains metallic sodium and is highly exhausted, for the vapour loses its rotating power when mixed with an inert gas. If we set the second nicol for extinction, the spectrum of the crater of the arc-lamp disappears, but on heating the tube and exciting the magnet, a vast number of bright lines appear in the red and green-blue regions of the spectrum. Spectra obtained in this way, since they are radically different from spectra of other types, I have named "magnetic-rotation spectra." Macaluso and Corbino observed the effect at the D lines, employing a sodium flame between the poles of a magnet, but they missed the complicated bright-line spectra which only appear when very dense sodium vapour is formed in vacuo.

In the case of the rotation for wave-lengths in the vicinity of the D lines, there is no difficulty in determining the. direction, i.e., whether positive or negative, for the broad bands of rotated light which border the absorption-lines can be moved from side to side by slight rotations of the analysing nicol; or we may employ the device so frequently used, the Fresnel double prism of right- and left-handed quartz, which tells us at a glance the direction of the rotation. In the case of the narrow lines of the channelled spectra, no information can be gathered as to whether the rotation is positive or negative by rotating the analysing nicol, for the smallest possible turn from the position of extinction causes the continuous spectrum to brighten up, obliterating the rotation lines. It is, however, of the utmost importance to determine the nature of the rotation in this case, as it will furnish many additional clues to the structure of the atom. An attempt was first made to employ metallic arcs in place of the white-hot crater, as the source of the light, on the chance that some of the lines might be of the right wavelength to suffer rotation in the region of the channelled spectra. If any of the lines were found to be rotated by the vapour, the direction of the rotation could be easily determined by rotating the analysing nicol until they were extinguished.

No lines were found, however, which had just the right wave-length. It then occurred to me that the selective rotatory power of the vapour could be utilized to furnish a source of light made up of just the right wave-lengths; in other words, magnetized sodium vapour between crossed nicols could be used as a light filter. The light passed by the crossed nicols when the magnetic field was excited was accordingly sent through another magnetized tube of vapour and examined with a third nicol and spectroscope. It was hoped that by setting the third nicol for extinction, and causing the bright-line spectrum to appear again by excitation of the second magnet, it would be possible to determine the direction of rotation of the lines by observing in which direction it was necessary to rotate the third nicol in order to blot them out. The first magnet, with its sodium tube and polarizing prisms, delivers plane-polarized light of exactly the wave-lengths of the bright lines of the magnetic-rotation This light is then passed through a second magnetized tube of sodium vapour, a nicol prism, and a spectroscope. The nicol having been set for extinction the bright-line spectrum disappeared, reappearing again as soon as the magnet was excited. It was found, however, that rotation of the third nicol was wholly without effect on the appearance of the lines, notwithstanding the fact that the light was originally plane-polarized. The magnetized sodium vapour appeared to have completely depolarized the light. The cause of this phenomenon is not difficult to explain. The lines which make up the magnetic-rotation spectrum, though they appeared as narrow as the iron arc-lines in a photograph which I made two years ago with a concave grating of 12 feet radius, are not in reality monochromatic. The action of an absorption-line is to rotate the plane of polarization of waves of nearly the same wave-length through various angles depending on their proximity to the absorptionline. It is these waves which are transmitted by the nicol. The line therefore has a finite, though narrow, width, and the second tube of magnetized vapour rotates the monochromatic constituents, of which the line is made up, through various angles. Some of the light in the line is therefore passed by the third nicol in every position.

From their analogy to the bright rotated lines which border the D lines when examined under similar conditions, we should expect all of the lines of the magnetic-rotation spectrum to be double, and I have spent a good deal of time in attempts to show their duplicity, using an échelon grating.

No very definite results were obtained, however, and more recent experiments show pretty conclusively that the rotatory power of most of the absorption lines is confined to wavelengths on one side of the line only. This same action is observed in an exaggerated degree by the ultra-violet absorption-line of mercury ( $\lambda = 2536$ ) which, as I have shown in a previous paper (Astrophys. Journ. July 1907), broadens very unsymmetrically. The form of the absorption-curve, and the magnetic rotation as shown with the Fresnel rotating quartz prisms, is shown in Pl. XIV. fig. 1,  $\alpha$  and b. The spectrum obtained by passing white light through the vapour placed between crossed polarizing prisms is shown in fig. 1 c, the fainter line being rotated 270°.

The behaviour of mercury vapour will be fully treated in a subsequent paper, and for the present we need only remark that an absorption-band is possible which only gives an appreciable magnetic-rotation for wave-lengths bordering it

one side.

This shows us that the lines of the magnetic-rotation spectrum would not necessarily appear double, even with the highest resolving powers (neglecting rotations larger than 90°). Though the lines appear as narrow as arc-lines even with a large grating, the magnetized sodium vapour and polarizing prism show us that in reality each line embraces a narrow range of the spectrum, the individual components of which are rotated through very different angles by the

vapour.

The experiment which finally showed clearly the nature of the rotation was made with a pair of Fresnel quartz-prisms. They were much thinner than those usually employed, as it was felt that it would be better to work with a single broad band of extinction, than a large number of parallel bands. The magnetically rotated lines are faint in comparison with the continuous spectrum from which they are derived, and it is consequently important to have the background upon which they are to show up as dark as possible. With a thick Fresnel prism we have the continuous spectrum at its full intensity traversed by a number of parallel dark bands, which correspond to the points on the slit at which the plane of polarization is parallel to the plane of extinction (long diagonal) of the analysing nicol, which is placed immediately behind the slit. There is in consequence more or less diffused light from the grating, which renders the background (the dark bands), upon which the rotated lines are to appear, much too luminous. To get rid of this effect, the best method is to use a thin prism, and cover the slit except for a small portion immediately above and below the single dark band of extinction.

With this arrangement of the apparatus the magnetically rotated line should penetrate the dark band from above or below, according to whether the rotation is positive or negative. If we excite the magnet and gradually heat the sodium tube, we see sharp needles of light shoot down from the continuous spectrum into the dark region immediately to the right and left of the D lines, as has been described by Macaluso and Corbino, Zeeman, and others. If we reverse the magnetic field the needles of light shoot up from below. The direction in which the plane of polarization is rotated by the D lines indicates that they are caused by vibrations of negative electrons. The important question to be answered is whether the absorption-lines of the band-spectra rotate the plane of polarization in the same or in the opposite direction, and whether they all behave alike.

The magnetic-rotation spectrum being much brighter in the red and orange than in the green and blue region, the first observations were made in this part of the spectrum. The spectroscope was a medium-sized instrument, consisting of a telescope and collimator of about 180 cms. focus,

furnished with a plane grating.

The sodium tube was heated until the fine black absorptionlines in the red appeared distinctly in the continuous spectrum above and below the horizontal dark band due to the Fresnel The current was then thrown into the magnet, the self-induction of which is so great that the field does not rise to its full intensity for several seconds, so that there was plenty of time to see exactly what happened. As soon as the switch was closed numerous needles of light commenced to penetrate the dark region, some of them shooting down from above, others shooting up from below. Of these, some only extended halfway or less across the dark band, while others crossed it completely. On opening the switch the luminous needles slowly withdrew from the dark background into the bright region from which they came, reminding one of the tentacles of an alarmed hydroid. The phenomenon is one of the most beautiful that I have seen for some time, for it shows us at once that some of the absorption-lines rotate the plane of polarization in the positive direction, while others rotate it negatively.

A very satisfactory photograph of the phenomenon was obtained on a Wratten and Wainwright panchromatic plate

with an exposure of one hour. An enlargement was made of the plate, which is reproduced in fig. 2a. Fig. 2b is a contact print from the original negative, and fig. 2c is a print from a plate made with a small two-prism spectroscope, showing the entire visible spectrum and the phenomenon at the D lines. It will be observed that in the case of some of the lines the bright needles of light have withdrawn almost entirely from the absorption-spectrum, leaving a dark line. (Compare the upper and lower spectra at the points indicated by the arrows.)

If the positive rotation at the D lines can be used as an argument that they are due to negatively charged electrons, it appears to me that the two types of rotation in the channelled spectrum is an evidence that we have both positive and negative electrons in the atom. It is perhaps unwise to speak of a positive electron, since electron has come to mean the disembodied negative charge, after it has

been expelled from the atom.

Whether the two types of magnetic rotation proves the existence within the atom of both positively and negatively charged discrete particles is for the theoretical physicists to answer. The observations recorded in this paper merely prove that some of the absorption-lines give a rotation

opposite to that given by the D lines.

Becquerel has inferred the existence of positive electrons in certain crystalline minerals, from the change in the appearance of the absorption-band when the crystal is placed in a magnetic field. The conditions in this case are, however, much more complicated than in the case of sodium vapour, for he is dealing with molecules of the rare earths in combination with or imbedded in other substances.

It will be extremely interesting to determine the direction of the rotation of the lines in the green and blue region, for these have been found to coincide with the regularly spaced series of lines in the fluorescence spectra excited by monochromatic radiations \*. I am now investigating this subject in collaboration with Mr. Felix Hackett, Fellow of the Royal University of Ireland.

<sup>\*</sup> See previous paper on "The Fluorescence and Magnetic Rotation Spectra of Sodium Vapour, and their Analysis." Phil. Mag. Nov. 1906.

### XXIV. On the Atomic Weight of Radium. By Henry Wilde, D.Sc., D.C.L., F.R.S.\*

In my paper read before the Society last year †, it was shown from the relations of the specific gravities of the alkaline-earth metals to their atomic weights, and also from the similar relations of the series of alkaline metals, that radium would have a proximate specific gravity of 5, and an atomic weight of 184, notwithstanding the assertions that have been made that the new element would be a heavy metal comparable with thorium (sp. gr. 11) and uranium (sp. gr. 18), and that its atomic weight ranged between 225 and 258. It was also shown that the atomic weights of the two series Hn and H2n of my tables, are definite multiple differences and not intermediate numbers.

In the several accounts which have been given of the atomic weight of radium, it is stated that the experimental determinations were made with radium chloride. Now it is well known to chemists that the series of alkaline metals and alkaline-earth metals, magnesium, calcium, strontium, and barium, unite with chlorine in one proportion only.

An important gain to chemical science which the multiple differences of the atomic weights have led up to, is the quantitative determination of the combining proportions of new elements in anticipation of the experimental results.

Taking the instance of radium chloride, I have estimated its combining weight after the classical method of Marignac‡ and Dumas § in their experimental determination of the atomic weight of barium as follows:—

- 1. One part of silver corresponds to 1.176 parts of radium chloride, or  $\frac{1.000}{1.176}$ .
- 2. The atomic weight of silver being 108, we have radium chloride=1·176 × 108=127 minus Cl (35)=92 the combining weight of radium with chlorine.
- 3. Now  $2 \times 92 = 184$  is the bivalent atomic weight of radium with bivalent oxygen in the positive and negative series H2n, as shown in my general Table, with a possible increase of one unit in the experimental determination, as in the instance of barium (136-137).

<sup>\*</sup> Reprinted from the Memoirs and Proceedings of the Manchester Literary and Philosophical Society, vol. lii. pt. 1 (1907). From a separate copy communicated by the Author.

<sup>†</sup> Manchester Memoirs, vol. li. No. 2 (1906).

<sup>‡</sup> Bibl. Univ. Archives, 1858, p. 81.

<sup>§</sup> Ann. Chim. Phys. vol. lv. p. 139 (1859).

Hn.	H2n.
$H = 1 \text{ Diff.} \\ -6$	He = 2 Diff. - 6
0 . 0 . 7 Li = 7 059† 7* -16	0 . 0 . 8 = Gl = 8 1.64? 9.2 -16
$1 \times 23 \cdot 0 = $ Na = 23 $0^{-98}$ $^{23}$ $-16$	$1 \times 24 - 0 = Mg = 24$ $1.74$ $-16$
$2 \times 23 - 7 = \text{Ka} = 39$ $0.86  39$ $-23$	$2 \times 24 - 8 = $ Ca = <b>40</b> $1.58$ $40$ $-24$
$3 \times 23 - 7 = Cu = 62$ $8.9  63.3 - 23$	$3 \times 24 - 8 = $ Zn = <b>64</b> $7 \cdot 2$ $65$ $-24$
$4 \times 23 - 7 = \text{Rb} = 85$ $1.52  85$ $-23$	$4 \times 24 - 8 = Sr = 88$ $2.54  87.5 - 24$
$5 \times 23 - 7 = Ag = 108$ $10.6  108$ $-23$	$5 \times 24 - 8 = Cd = 112$ $8^{69}$ $112$ $-24$
$6 \times 23 - 7 = \text{Cs} = 131$ $1.88  132$ $-23$	$6 \times 24 - 8 = $ Ba $= 136$ $3.75$ $137$ $-24$
$7 \times 23 - 7 = -154$ $12 \cdot 27$ $-23$	$7 \times 24 - 8 = - = 160$ $10.13 \updownarrow$ $-24$
$8 \times 23 - 7 = - = 177$ $= -23$	$8 \times 24 - 8 = \text{Ra} = 184$ $5.0  1$ $-24$
$9 \times 23 - 7 = \text{Hg} = 200$ 13.6 200	$9 \times 24 - 8 = Pb = 208$ 11·44 207

<sup>\*</sup> Accepted Atomic Weights. † Specific Gravities. ‡ Estimated.

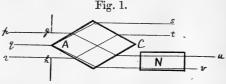
I have previously shown that the positive series of elements H2n closes with lead (208), and that if any higher member of the series of alkaline-earth metals exist, it would have an

atomic weight of 232, and an approximate specific gravity of 7\*.

Assuming this hypothetical member to be radium, the combining equivalent of its chloride with silver (Cl 35 and Ag 108) would be 1.399 in accordance with the determinations arrived at with the other members of the same series, and not 1.371 as determined experimentally for the intermediate atomic weight 226, recently assigned to radium †.

XXV. A New Spectrophotometer of the Hüfner Type. By ROBERT A. HOUSTOUN, Ph.D., D.Sc., Assistant to the Professor of Natural Philosophy in the University of Glasgow‡.

URING the past forty years a great number of different spectrophotometers have been worked out. This will readily be seen by a reference to Kayser's Spectroscopie, vol. iii. chap. 1, where a complete list is given §. although so much attention has been given to designing and testing new instruments, few spectrophotometers have been made, and most laboratories are without one. This must in part be ascribed to their cost, and also to their construction, which usually prevents them from being used for any other The object of the present paper is to describe an attachment which may be fitted to any spectrometer or spectroscope, converting it into a spectrophotometer, and which may be removed at once when the ordinary use of the instrument is desired. A method for applying the instrument to the measurement of absorption in the ultra-violet is also described.



The Hüfner Spectrophotometer || consists (fig. 1) of a spectroscope, before the slit of which a Glan-Thompson prism

\* Manchester Memoirs, vol. li. No. 2 (1906). † Comptes Rendus, vol. cxlv. p. 422 (1907). † Communicated by Professor A. Gray, F.R.S.

§ This list does not mention the new form of the König spectrophotometer designed by Dr. Martens ("Ueber eine Neukonstruktion des Königschen Spektralphotometers," F. F. Martens u. F. Grunbaum, Ann. der Phys. xii. p. 984, 1903), and the spectrophotometer of Dr. J. Milne ('Nature,' lxxii. p. 391, 1905).

"Ueber ein neues Spectrophotometer" von G. Hüfner, Zs. f. physic.

Chemie, iii. pp. 562-571 (1889).

N and a glass rhomb AC—the Hüfner rhomb—is brought. The edge A is ground very sharp and bisects the slit gh. If we disregard the polarizing effect of the rhomb, the upper beam bounded by the rays sAq and thr, which illuminates the lower half of the slit, consists of natural light, and the beam bounded by the rays ugp, vAq, which illuminates the upper half of the slit, consists of light polarized in either a vertical or horizontal plane. Another nicol is inserted in the path of both beams. If we look into the eyepiece, we see two spectra, one above the other, and by rotating this

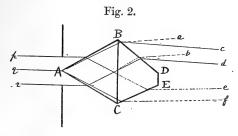
nicol we can alter their relative intensity.

The light which comes from the upper half of the slit must be plane-polarized before entering the second nicol, and the light which comes from the lower half of the slit must be unpolarized natural light. But it is partially polarized by both the Hüfner rhomb and dispersion-prism. Hüfner was perfectly aware of this, and in his improved instrument made by Albrecht he got over the difficulty by choosing the glass and angle of the dispersion-prism so that it removed the polarization produced by the rhomb (cf. article cited, p. 564). Messrs. Hilger have apparently rediscovered the same method of removing the polarization produced by the rhomb, and it is described at length by Mr. F. Twyman\* under the impression that it is new.

Any dispersion-prism will not do then. Its angle must be chosen so as to remove the polarization produced by the

rhomb.

I have recently designed a prism which performs the functions of both the rhomb AC and the Glan-Thompson prism N, but which polarizes both beams in planes at right angles to one another, and thus can be used with any dispersion-prism whatever (fig. 2).



ABC is made of glass  $\mu_D = 1.526$ , the sides AB, BC, CA

<sup>\* &</sup>quot;Improvements in the Hüfner type of Spectrophotometer." F. Twyman, Phil. Mag. April 1907.

being each 2 cms. long. It is cemented to a prism of Iceland spar, BDEC, cut with its axis perpendicular to the plane of the paper. The angle D is 127° 12′, E is 115° 49′, and BCE is 36° 44′.

The action of the prism may be better understood by considering the beams of light to go in the reverse direction—from the object-glass of the collimator to the slit. The beam qr is broken into two by the Iceland spar prism, cd being the ordinary beam and ab the extraordinary. The beam pq is broken into two, but only the extraordinary ef emerges, the ordinary being totally reflected at the surface CE. The beams ef, cd meet 15 cms. out in an elliptical spot of light measuring 2.0 by 2.4 cms., the long axis being vertical. The beam ab is quite 2 cms. clear.

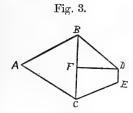
If now we have as source of light an incandescent mantle behind a screen, with an aperture at the proper place not much larger than 2.0 by 2.4 cms., and if we look into the eyepiece, we see two spectra one above the other and polarized at right angles to one another. The ordinary component of the lower beam misses the slit entirely, the extraordinary component of the upper beam misses the object-glass of the collimator.

The prism was fixed in a rectangular brass cell open at the ends with the edge A protruding. The brass cell was mounted in a short piece of brass tubing with a milled head, which turned inside another piece of brass tubing fixed in front of the slit. The prism could thus be rotated about the axis of the collimator—the only adjustment necessary. The inner tube containing the cell could be removed when required, the outer tube remaining fixed to the slit. When it was returned to its plane the milled head prevented it sliding in too far and damaging the edge A. The prism was attached to one of W. Wilson's well-known College spectrometers.

All that is then required to complete the equipment of the instrument as a spectrophotometer is one of the nicol-prism polarizers with a divided circle, which is supplied by the makers to fit over the object end of the collimator. This is preferable to the object end of the telescope as it avoids the depolarizing effect of the dispersion-prism. The eyepiece supplied with the instrument for ordinary use magnifies, however, too strongly, when it is used as a spectrophotometer.

Much the better place for the nicol, however, is the eyepiece. In spectrophotometry it is necessary to waste as little light as possible. The object-glasses of collimator and telescope had a clear aperture of one inch. A nicol with an aperture of one inch would be too expensive, and makers usually fit a much smaller nicol, thus causing a large loss of light. In the eyepiece the rays come closer together, and a smaller nicol may be used. An ocular nicol with divided circle, reading telescope, and screens for cutting out the regions of the spectrum not under observation was therefore made by F. Schmidt and Haensch, Berlin, to replace the ordinary eyepiece. The prism for attaching to the slit was made by R. & J. Beck, Ltd. Its angles do not require to be made accurately, the only point necessary being that the axis of the Iceland spar should be parallel to the edge A. It is extremely important that the slit prism be set with the axis of the Iceland spar perpendicular to the refracting edge of the dispersion-prism. If that is not the case, the two beams are not polarized in and perpendicular to the plane of incidence when they enter the dispersion-prism. planes of polarization will then be rotated, and the positions in which the ocular nicol extinguishes the upper and lower spectra will not be at right angles to one another. The correct position of the slit prism may thus be found by trial.

If it is preferred to keep the one beam unpolarized, as in the ordinary Hüfner spectrophotometer, then a prism of the form shown in fig. 3 might be used. ABC and BFD are



glass, FDEC is Iceland spar. There is now no light lost by reflexion in the nicol. Owing to the space saved, wider cells might be used and the absorption of more dilute solutions measured.

The limitation of the size of the aperture causes no difficulty

in practice.

With reference to the accuracy obtained, it is not possible with a Hüfner rhomb to get the two spectra under comparison to touch one another so sharply as in the case of a Lummer-Brodhun cube or a biprism such as is used in the Kœnig-Martens spectrophotometer, as my experience of the

Phil. Mag. S. 6, Vol. 15, No. 86, Feb. 1908.

latter instrument has shown me\*. The latter instrument also has the advantage that the polarizing prism is placed after the dispersion-prism and the error due to depolarized light removed. In practice, however, since twice as much light is lost in the latter instrument, the Hüfner spectrophotometer is as accurate, and is of course simpler. The University of Glasgow possesses a Wild spectrophotometer, but so much light is lost in the latter instrument that in accuracy it is very much inferior to the others.

To test the possibilities of the instrument for spectrophotometry in the ultra-violet, I attempted to measure the absorption of copper sulphate photographically. Copper sulphate was chosen because it is a salt for which accurate values are given in Landolt and Börnstein's tables. It absorbs the red end of the spectrum, but the results show that rough quantitative work in the ultra-violet could be done very

easily.

A nicol was attached to the end of the collimator. The diameter of its aperture was less than one quarter the diameter of the lens, and hence there was a great loss of light. In place of the telescope there was placed a camera, the focal length of its lens being about 51 cms. Wratten and Wainwright's panchromatic plates were used. The spectrum from 6700 to 3500, where the absorption of the glass begins, was taken at one exposure and measured more than 5 cms. in length.

First of all both beams were left free and the nicol set so that its plane of polarization made angles of 55°, 52°, and 50° with the plane of polarization of the lower beam. At 52° the one spectrum was brighter, at 50° the other, so 51° was taken to be the angle at which the nicol would be set for equal brightness. A photograph was then taken of the flame spectrum of Li, K, Na, and Th, and the wave-length of a point of the plate determined in terms of its distance

from the D lines.

Then the cell with the copper sulphate was placed in position, and exposures made for different positions of the nicol. A bunsen flame with a sodium bead was placed between the incandescent mantle and the cell. The sodium line appeared therefore on all the plates. The distance of the point on the plate where the two spectra touching one another were equally black was measured from the D line, and the wave-length of the point could thus be determined.

<sup>\* &</sup>quot;Untersuchungen über die Absorption des Lichtes in isotropen Körpern," R. A. Houstoun, Ann. der Physik, xxi. p. 535 (1906).

If a gives the position of the nicol, the fraction of the intensity of the incident beam transmitted by the solution is given by

$$I = I_0 \frac{\tan^2 \alpha}{\tan^2 51^\circ}.$$

Fig. If c denote the concentration of the solution in grammolecules per litre, and d the thickness of solution passed through, then A the "molecular extinction coefficient" is defined by

$$I = I_0 10^{-Acd}$$
.

The following table gives the results:-

α.	Time of exposure.	λ.	A.	A from the tables.
49.8	10 mins.	4750	0.053	0.009
47.4	37	5640	0.187	0.29
45.0	. ,,	5710	0.322	0.37
41.6	,,	5850	0.514	0.57
38.1	27	5980	0.714	0.83
30.0	15 mins.	6130	1.22	1.24
23.1	20 mins.	6200	1.69	1.50
14.9	39	6410	2.45	2.42

c = 0.5424 gm.-molecules/litre.

d=1 cm.

The width of the D line on the plates is 0.6 mm.

One exposure gives A for only one wave-length, but if the absorption had more than one maximum the exposure might give A for several values of  $\lambda$ . The values of A taken from the tables are of course more accurate. I attempted to determine the wave-length by putting a piece of didymium glass before the slit, but this method was not so accurate as the one used.

The cost of the instrument has been borne by the Carnegie Trust for the Universities of Scotland.

# XXVI. Note on X-Rays and Scattered X-Rays \*. By Charles G. Barkla, M.A., D.Sc.†

IN a paper on Polarized Röntgen Radiation ‡ I showed that on the æther-pulse theory of Röntgen rays, we should expect the primary beam proceeding from an X-ray tube in a direction perpendicular to that of propagation of the cathode stream to be partially polarized, and on the theory of scattering by electrons in light atoms the secondary rays proceeding in a direction perpendicular to that of propagation of the primary, from substances of low atomic weight, ought to be almost completely plane polarized. Experiments were described which in both cases demonstrated the polarity &, and the effects were shown to be of the order of magnitude expected on these theories. The evidence in favour of the theories appeared so strong, that a more complete study of the distribution of intensity of the secondary radiation was considered unnecessary and unimportant. Prof. Bragg, however, in a recent paper | regards some of the evidence in favour of the æther-pulse theory as a little over-rated, and proposes in its place the hypothesis that an X-ray beam consists mainly of "neutral pairs" (each consisting of a positive and a negative particle rotating in a plane containing the direction of propagation of the "pair"). This he considers affords an easier explanation of the phenomena of X-rays and is not improbable a priori.

It appears altogether unnecessary to fully discuss such an hypothesis, for the study of the distribution of intensity of secondary radiation from light atoms affords a simple and apparently conclusive test between the æther pulse and the "neutral pair" theories. At the same time this makes the investigation on polarization more complete, and furnishes a delicate method of testing the presence of scattered rays in

a complex radiation.

According to the æther-pulse theory of Röntgen rays, when a primary pulse passes over an electron in a light atom, the electron is accelerated in a direction opposite to (being charged negatively) the direction of electric intensity in the

+ Communicated by the Author.

<sup>\*</sup> The expenses of this Research have been partially covered by a Government Grant through the Royal Society.

<sup>†</sup> Phil. Trans. A. vol. cexiv. 1905, pp. 467-479. § Royal Soc. Proc. A. vol. lxxvii. 1906, pp. 247-255. || Phil. Mag. [6] vol. xiv. Oct. 1907, pp. 429-449.

pulse. During the passage of an unpolarized primary beam, these accelerations are uniformly distributed in direction in a plane perpendicular to that of propagation of the beam.

Now the electric intensity at a point P in one of the

resulting secondary pulses is expressed by  $\frac{ef \sin \theta}{r}$ , where

e is the charge and f the acceleration of the electron, r the distance from the electron to the point P, and  $\theta$  the angle which the line joining the electron to the point P makes with the direction of acceleration.

If P is on the line of propagation of the primary pulse

over the electron  $\theta = \frac{\pi}{2}$ , and the intensity  $= \frac{ef}{r}$ .

If P is in the plane through the electron perpendicular to the direction of primary propagation,  $\theta$  varies uniformly from 0 to  $\pi$  for the primary pulses.

The intensities of radiation then in these two directions

are proportional to

$$\Sigma \frac{e^2 f^2}{r^2}$$
 and  $\Sigma \frac{e^2 f^2 \sin^2 \theta}{r^2}$  respectively.

When the primary beam is unpolarized, the average value of  $\sin^2 \theta = \frac{1}{2}$ , consequently the intensity of secondary radiation in the direction of propagation of the primary is double that in a direction at right angles.

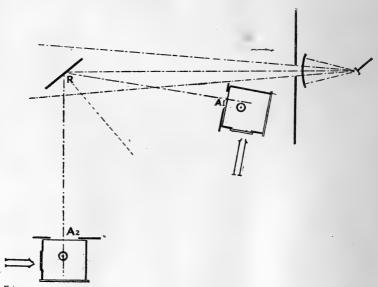
On the neutral pair hypothesis it is supposed that a pair which strikes a substance consisting of light atoms is liable to be taken up only by an atom revolving in the same plane. It is sometimes ejected again, and its subsequent rotation and translation continue to take place in the one plane; therefore all pairs ejected in any direction at right angles to that of propagation of the primary rotate in the plane of primary and secondary propagations. A tertiary beam is therefore strongest when in the same plane. This is Bragg's explanation of the polarization of the secondary beam as shown by the tertiary beams.

The results of experiments described below, however, show that this cannot be the true explanation of the polarization effect; neither is the theory capable of explaining the partial polarization of the primary. It is easily seen that on this hypothesis all the possible planes of rotation of pairs in a primary beam contain the direction of propagation of that beam, and therefore that any pair has a chance of being

ejected again along that axis. If we consider the radiating mass at the centre of a sphere with the direction of primary propagation as the axis, then the different possible planes of ejection are the planes through this axis, and as in each plane we may assume there is equal chance of ejection in all directions, the number of pairs received by any element of surface of the sphere is proportional to the density of the lines of longitude on that element. This varies as the secant of the latitude from 1 at the equator to infinity at the poles. The total energy of radiation received by a small area near the poles is therefore many times as great as that received by a similar small area near the equator; that is, a small beam of secondary rays proceeding in a direction near that of propagation of the primary, is many times as intense as one in a direction approximately at right angles to this.

To test between these theories, the simple apparatus was

arranged as shown in the diagram.



A narrow pencil of X-rays emerged through a small circular aperture of 85 cm. radius in a lead box, and at a distance of 38 centimetres in this pencil a square slab of carbon ( $8\times8$  cm.) was placed in a vertical plane with its face equally inclined to the lines joining its centre to the centres of two equally distant rectangular apertures  $A_1$  and  $A_2$  in lead screens. Behind these were situated electroscopes

of the type described in previous papers—modifications of those devised by C. T. R. Wilson. Their thin paper and aluminium faces were against the apertures, which were of dimensions  $3.2 \times 5$  cm. and  $5 \times 5$  cm., and were placed symmetrically with regard to the carbon at a distance of 27 centimetres.

With this arrangement the radiation from each atom before entering one electroscope had to travel approximately the same distance in carbon and air as that entering the other. The intensities of the secondary beams entering the electroscope were then proportional to the intensities of radiation from the atoms in the two directions  $RA_1$  and  $RA_2$ . One of these  $RA_1$  made only a small angle with the axis of the primary beam, while the other  $RA_2$  was perpendicular to that axis.

By first placing a sheet of copper in the position R, it was found, by alternately placing one electroscope in the two positions A<sub>1</sub> and A<sub>2</sub>, that there was no appreciable difference between the intensities of secondary radiation from copper in the two directions.

This is what was expected from the results of previous experiments on copper, for it was found that when a polarized primary beam fell on copper the intensities in the two principal directions at right angles were equal, indicating that the copper radiation was equally intense in all directions whatever the position of the plane of polarization and direction of incidence of the exciting primary beam. The character of the secondary radiation from copper had also been shown to be approximately independent of that of the primary producing it. The equally intense copper radiations were therefore used to standardize the two electroscopes afterwards used in place of the one.

Thus in one experiment after correction for the normal ionization in the electroscopes, for the effects of the secondary rays from air and for the ionization that may have been produced by very penetrating primary rays in the electroscopes, the deflexions of electroscopes  $A_1$  and  $A_2$  were 12.5 and 18.05 respectively when copper was the radiating substance. Now as these were due to equally intense beams, the deflexion of 12.5 in electroscope  $A_1$  was equivalent to 18.05 in  $A_2$ . When the copper was replaced by carbon the deflexions were 7 and 5.2 respectively, and by repeated observations 7.9 and 5.95. Taking the average of these we have 7.45 and 5.575. If the electroscopes had been equally

i.e.

sensitive the ratio of deflexions would therefore have been

$$\frac{7.45 \times 18.05}{12.5} : 5.575.$$

$$10.76 : 5.575$$

$$1.93 : 1.$$

That is, the average intensities of the secondary beams from R received by the electroscopes  $A_1$  and  $A_2$  were in the ratio 1.93:1.

As this ratio appeared to vary considerably in different experiments by an amount much greater than the possible experimental error would account for, it was apparent that it depended to a certain extent on the character of the primary radiation.

Gas was therefore admitted into a regulating X-ray tube, until it was brought to that state when a discharge through it did not produce X-rays which could be detected by the electroscopes at all. A discharge was then passed through until rays were emitted in sufficient intensity to be experimented upon. The ratio of intensities was then found to be 2.0:1. When the bulb was somewhat "harder" this became 1.93:1, and when "harder" still the ratio became 1.80:1. In order to experiment on a beam of much greater average penetrating power, the more absorbable portion of this beam was then cut off by a plate of aluminium '04 cm. in thickness. This diminished the ionizing power of the primary to about 30 per cent. of its original value, while the transmitted beam was on the average about twice as penetrating. Using this penetrating primary beam, it was found that the ratio of intensities had dropped to 1.51:1.

These experiments were repeated with other X-ray tubes and the results were confirmed, the ratio never exceeding 2:1, and decreasing with increasing penetrating power of

the primary rays used.

It must, however, be observed that the primary beam used in these experiments was partially polarized, the variation in intensity of secondary beams from carbon in the two principal directions at right angles to the direction of primary propagation amounting to about 20 per cent. when the beam was of the very absorbable type, but only to 6 or 7 per cent.\* when the rays were much more penetrating. Thus the

<sup>\*</sup> There is, of course, probably no lower limit to the variation, but these were approximately the limits found for the different beams of the type used in these experiments.

intensity of the beam RA<sub>2</sub> depends to this extent on its position with regard to the cathode stream in the X-ray tube. The above ratios were obtained when the beam RA<sub>2</sub> was parallel to the cathode stream, and therefore have the maximum values. The intensities of secondary radiation in directions RA<sub>1</sub> and RA<sub>2</sub> when easily absorbed primary rays were used, were therefore in ratios varying from 2:1 to 2:1·2, i.e. from 2:1 to 1·66:1, according to the position of the plane of polarization of the partially polarized primary beam.

For an unpolarized primary beam, the ratio of intensities in the two directions RA<sub>1</sub> and RA<sub>2</sub> would therefore be

approximately 1.85:1.

The results of these experiments in this way showed that the ratio of the intensities of secondary rays from carbon in the two directions indicated varied from about 1.85:1 with very soft rays to about 1.45:1 for penetrating rays. Now the first ratio is of the order—probably a little less—that might have been expected if we assumed perfect scattering on the æther-pulse theory, the rays entering electroscope  $A_1$  making a small angle with the direction opposite to that of primary propagation, and most of those entering  $A_2$  being not quite perpendicular to the direction of propagation of the primary.

On the other hand, on the neutral pair hypothesis the ratio should be roughly 7 or 8:1. This, however, is on the assumption that a pair rotating in one plane continues even after ejection from an atom which it strikes to rotate accurately in the same plane. If we admit any deviation from this, then the ratio of intensities becomes less than the above. But the polarization which exists in a secondary beam from carbon is sufficiently complete to show that if the effects are to be explained on such an hypothesis, the behaviour of the pairs must approximate very closely to this ideal, and consequently the ratio of intensities in the two directions  $RA_1$  and  $RA_2$  could not possibly have been lower than 4:1 or 5:1.

We thus have what appears to be most conclusive evidence against the "neutral pair" hypothesis, and the most convincing verification of the æther-pulse theory that could be

given by such experiments.

Not only is there perfect agreement between theory and experiment here, but experiments showed that where the secondary rays were otherwise found to be less purely a scattered radiation judged by their penetrating power, and by polarization experiments, there was also a reduction of the ratio of intensities discussed in this paper—the result to be expected on the pulse theory.

Thus:-

Using the rays which are emitted by an X-ray tube in which the pressure is as high as possible when producing X-rays of appreciable ionizing power, the absorbability of the secondary rays from carbon differs exceedingly little if at all from the primary. Direct experiments did not indicate the slightest difference.

Using such a beam as the primary to be tested for polarization by study of the intensities of secondary radiation from carbon, the maximum amount of polarization of a primary was observed—about 20 per cent. variation. When such a primary was used to produce a secondary beam from carbon, the secondary beam was found by a study of the tertiary rays to be fairly completely polarized.

When such a primary beam was incident on carbon, the ratio of the intensities of secondary radiation in the direction opposite to that of propagation of the primary and in a direction at right angles was very close to the theoretical value for perfect scattering, i. e. 2:1 (within 5 per cent.).

As the primary rays became more penetrating, the difference in the ionizing powers of the primary and secondary beam from carbon became more marked; the difference in their penetrating powers increased; the evidence of polarization of the primary became less pronounced\*; and the ratio of intensities of secondary radiation opposite to and perpendicular to the direction of primary propagation decreased.

According to this theory, then, all those substances of low atomic weight—up to and including sulphur—when subject to "soft" X-rays should emit secondary rays varying in intensity in the two directions approximately in the ratio 2:1. It is possible, I think probable, that the behaviour of sulphur varies much more rapidly with a variation of the penetrating power of the primary than any of the others, and that for some primary rays this ratio of intensities may be very different from that found by experiments on the lower part of this group.

Paper, when tested in the same way as carbon for "soft" rays, gave off radiation whose intensity was found to vary in the ratio 2.01:1, which again after correction shows the true ratio of intensities not appreciably different from that for the "softest" rays from carbon.

\* This might possibly be due to the penetrating primaries actually being less polarized, but when considered with other changes it appears probable that much of the decrease of observed polarization is due to the secondary beams not consisting of purely scattered rays, and so not showing the polarization. The best results showing polarization in the secondary beam were always obtained by using easily absorbed rays.

Though accurate experiments were not made on aluminium,

it was found to behave in the same way.

The penetrating power of the principal portion of the secondary radiation from Cr, Fe, Ni, Co, Cu, Zn has been found to be entirely different, being almost if not quite completely independent of the penetrating power of the primary producing it. The origin of the radiation will be discussed The intensity from one of these we should expect elsewhere. not to depend on the direction of propagation of the primary. This is what was found for the radiation from copper. When, however, the behaviour of iron was compared with that of copper, it was invariably found that the ratio for iron was greater than that for copper. This is shown below. The three comparisons were made at different times. appears to indicate a small amount of scattered radiation, though possibly not more than 2 per cent. of the total radiation from each atom.

Radiator.	Time.	Corrected deflexion of A <sub>1</sub> .	Corrected deflexion of $\mathbf{A}_2$ .	Ratio of deflexions $A_1: A_2$ .	Ratio of intensities of $RA_1$ and $RA_2$ .
Cu	40 secs.	22·3	29·8	75:100	1:1
Fe	25 ,,	- 12	14·25	84:100	1:12:1
Cu	40 ,,	27·5	42·45	65:100	1:1
Fe	50 ,,	27·7	37·15	74:100	1·13:1
Cu		34·2	48·8	70:100	1:1
Fe		26·7	34·55	77:2:100	1·10:1

It seems quite possible from other considerations that a certain amount of scattered radiation does appear, as the atomic weight is getting near that for which a scattered radiation was found by much cruder methods.

Again, Ag, Sn, Sb, I, &c. belong to quite another class of substances, for the radiation from these depends to an extraordinary extent upon the character of the primary. It has been shown that when primary rays of moderate penetrating power are used, this secondary is not a scattered radiation, though from tin its average penetrating power may be very like that of the primary producing it; it is not polarized, and it does not give evidence of polarization in a primary where it exists. Though very different from the radiation from one of the elements in the Cr–Zn group, we should for these reasons expect the beam to show very little or no variation in intensity in the beams RA<sub>1</sub> and RA<sub>2</sub>. The results of comparisons with copper are given.

No. of Street, or other Persons and Street, o	Radiator. Time.		Corrected deflexion of A <sub>1</sub> .	Corrected deflexion of $\mathbf{A}_2$ .	Ratio of deflexions of $A_1$ and $A_2$ .	Ratio of intensities.
	Cu	60 secs.	33·32	60·67	54·9 : 100	1:1
	Sn	180 ,,	6·27	12·15	52·4 : 100	·95:1
	$\begin{array}{c} \mathbf{C}\mathbf{u} \dots \dots \\ \mathbf{S}\mathbf{n} \end{array}$	50 ,, 180 ,,	23·6 6·65	38·8 10·5	60·8 : 100 63·3 : 100	1:1 1:04:1
2	Cu	40 ,,	27·5	42·45	65 : 100	1:1
	Sn	240 ,,	13·6	20 5	66·3 : 100	1:02:1

From these experiments there was no indication of a decided variation; we conclude that there was equality of intensity in the two directions. Another group of substances classified according to their behaviour under X-ray transmission includes W, Pt, Pb, and Bi. These emit a radiation which appears to differ from that from any of the other groups referred to. When the radiation from lead was tested in a similar way, no evidence of scattering was obtained.

Experiments were also made to determine the behaviour of a number of these elements under more penetrating rays, but the conditions of experiments have not yet been varied sufficiently to lead to definite conclusions.

These results thus afford strong confirmation of the electromagnetic pulse theory of X-rays, and of the theories of scattering and of polarization based on this.

The method of comparing the intensities of radiation in the two directions indicated is a delicate one for detecting the presence of scattered rays, or of measuring the control over radiating electrons, exercised by the primary pulses while producing or stimulating the production of secondary rays.

producing or stimulating the production of secondary rays.

The scattering of "soft" X-rays by substances of low atomic weight has been shown to be almost perfect, and the appearance of a radiation which is very far from a purely scattered radiation, when more penetrating rays are used, has been shown in a very marked way. The small proportion of scattered rays in other secondary radiations has been demonstrated.

These experiments, however, do not show that under suitable conditions scattered rays may not be obtained from elements hitherto found to emit only an uncontrolled secondary radiation.

I wish to thank Mr. F. J. Thorpe, B.Sc., for assistance in conducting some of these experiments.

George Holt Physics Laboratory, Liverpool. XXVII. The Mixing of Gases.—Remarks on Mr. Burbury's regent Papers. By Prof. W. McF. Orr, M.A.\*

I BEG to make some remarks on the two papers by Mr. Burbury on the Diffusion of Gases which have

recently appeared in this Magazine +.

Mr. Burbury appears to dispute the propositions: (1) that when two gases mix by diffusion the process is an irreversible one; (2) that every irreversible process is attended by a loss

of available energy.

As regards the former proposition, Mr. Burbury, in the first paper, after discussing some points in the kinetic theory of gases, suggests ‡ that the diffusion would be reversible, provided the system were completely isolated, a condition which it is impossible to realize in nature, but admits that it is irreversible in any experiments that can practically be made. On this view, the point at issue may be said by one unfamiliar with the kinetic theory of gases to be an abstract question affecting a system under conditions so unnatural that, whichever way it is decided, it nevertheless allows the natural process to be, as a matter of fact, irreversible.

Mr. Burbury does not discuss the latter of the two propositions directly, but turns his attention instead to an equivalent theorem relating to increase of entropy, and merely for the particular case in hand, i. e., the diffusion of gases. On this point he urges & that there is no gain of entropy in any one collision between molecules, and that therefore no increase can result from all the collisions taken together. It may, I think, be fairly replied, again from a standpoint outside the kinetic theory, that it is quite unnecessary to consider such questions as this and others which he raises. The usual definition of entropy makes no reference to single molecules but deals with matter in bulk; the Kinetic Theory of Gases is an interesting annexe of Thermodynamics, but the latter in no way depends on the former; if the molecular theory gives results which contradict our experience, necessarily limited to that of gross matter, then, as happens from time to time with other branches of science, it requires revision, as regards logical development, or premisses, or both. Moreover, a being who could have experience of individual molecules would, in all probability, not understand the notions of pressure, temperature, heat,

<sup>\*</sup> Communicated by the Author.

<sup>†</sup> Phil. Mag. July and Sept. 1907.

<sup>1</sup> L. c. p. 125. § L. c. p. 124.

work, energy, &c., in the sense in which we adopt them; our distinction between heat and other forms of kinetic energy might seem to him specially artificial, and in this connexion it may be remarked that, although it is impossible to separate a mixture of (perfect) gases into constituents at the same pressure as the mixture, if the temperature is kept constant, without doing work on them, yet the gases give out in the process an equivalent quantity of heat, so that their energy remains unaltered.

The second proposition in all its generality, or the equivalent theorem concerning entropy, does not, indeed, appear to be formally deducible from any usually accepted statement of Thermodynamic laws; each may form his own opinion as to how far experience and experiment warrant its acceptance. I imagine, however, that it is admitted almost universally that every process occurring in nature is irreversible and also that it involves a loss of available

energy.

But in the particular case of the diffusion of gases, or at least of some gases, it is a fact established by direct experiment, and, I had supposed, beyond all dispute whatever, that there is a loss of available energy, a statement which Mr. Burbury appears to challenge \* (for the case of oxygen and nitrogen). Lord Rayleigh, in the opening paragraph of the paper to which Mr. Burbury refers in his second paper, called attention to this in 1875; and the rest of Lord Rayleigh's paper is devoted, not so much to a proof that there is such a loss, but to calculations of its amount. In the simple and common experiment there described, a tube containing hydrogen and closed at the upper end stands over water; the hydrogen escapes through the pores more rapidly than the air enters, thus creating a partial vacuum, and the water accordingly rises. The available energy is thus actually seen to be used, to some extent, in pumping water up a And, if we were able to separate the hydrogen glass tube. and the atmospheric air, in their original states, from the mixture, keeping the temperature constant, without doing work on the system—a process the possibility of which Mr. Burbury appears to suggest in his second paper †—it would be easy to devise a heat engine by which we could continue to pump water from a lower to a higher level, and in which the working substance would go through a closed cycle taking in heat at a constant temperature (atmospheric), but requiring no condenser,—thus obtaining a perpetual

<sup>\*</sup> L. c. p. 123. † L. c. p. 423.

motion of the second kind, as Ostwald and Planck call it; it seems unnecessary to describe a suitable arrangement in detail. There would, of course, be a loophole of escape if there were any reason to think that the energy is actually

drawn from the plug.

Mr. Burbury makes no allusion to this paragraph of Lord Rayleigh's, but proceeds to refer to one of the possible processes of separation of gases which Lord Rayleigh employed in calculating the amount of work necessary for the operation. In this it is supposed that a tall narrow vertical tube is mounted on a large reservoir containing a mixture of two gases at sensibly constant pressure: the composition varies in different parts of the tube, owing to the effect of gravity, there being a greater percentage of the lighter gas at the top of the tube than at the bottom. Lord Rayleigh supposes that a small quantity of gas is (1) removed from the top of the tube (an equivalent amount being, I take it, automatically supplied from the reservoir so that the composition of the gas at every point of the tube remains unaltered); (2) compressed until it attains the pressure of the gas in the reservoir; (3) allowed to fall to the level of the reservoir; and (4) forced into the reservoir, (but, as I understand it, kept separated from the gas in the reservoir by an impermeable membrane); the temperature is supposed to be constant throughout. Thus, from the original contents of the reservoir there has been separated a small portion of gas which is of a different composition from that which remains. Mr. Burbury, however, apparently ascribes to Lord Rayleigh a somewhat different process; he supposes each element of the vertical column, in succession, brought down to the level of the reservoir (but without being replaced by other similar elements and without being forced into the reservoir). This he describes as a partial separation of the gases, which appears to be a misdescription; it is merely an alteration in the position and density of gases without any change in the proportions of their constituents. He then regards these operations as the second half of a complete cycle of which he proceeds to supply the first half: evidently he does not use the phrase "complete cycle" in its usual sense. In this first half he supposes a tube, which is a facsimile of the vertical one, but placed horizontally at the level of the reservoir, to be filled with the reservoir gases, interchanges the molecules of the two gases in it until each element has the same constitution as the corresponding element of the vertical column, expands each element until it has the same pressure and density as the

corresponding element of the vertical column, and sets the tube vertical in a position corresponding to that of the column. When these operations are prefixed to those which he ascribes to Lord Rayleigh, a series of processes is obtained which, of course, might as well be terminated after the first, i. e., the partial separation of the gases in the horizontal tube; and Mr. Burbury contends that Lord Rayleigh has proved nothing inconsistent with the supposition that this separation -at constant pressure and constant temperature—can be performed without the expenditure of work. In one sense this contention may be admitted, for, if I apprehend the situation correctly, Lord Rayleigh's investigation is not directly relevant to the series of processes which Mr. Burbury describes. If, however, in the reservoir, a small portion of gas of the same constitution as that at the top of Lord Rayleigh's tube be separated from the remaining contents, and if this partial separation can be performed at constant temperature and constant pressure without doing any work on the gases, then, by reversing the processes which Lord Rayleigh, if I understand correctly, actually does employ, it follows from his investigation that the gas system would again constitute the working substance in a heat engine which contradicts the Second Law of Thermodynamics.

#### XXVIII. Intelligence and Miscellaneous Articles.

ON THE FOCOMETRY OF A CONCAVE LENS.

To the Editors of the Philosophical Magazine.

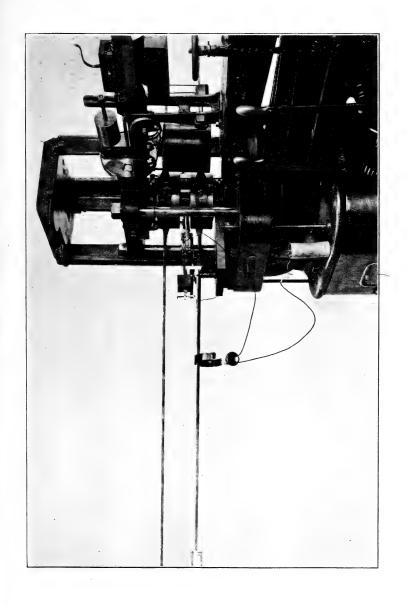
GENTLEMEN,-

IT has just been pointed out to me that the first method I described in the "Note on the Focometry of a Concave Lens" in the Philosophical Magazine for January, is given in the Syllabus of the Course of Practical Instruction in Physics at the Royal College of Science, London (1902).

I was, unfortunately, unaware of this at the time of writing, as it is not given in my copy, which is an earlier edition (1892). The second method is, of course, similar in principle to the first; while the third is derived from the second by reversing the direction

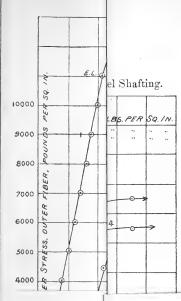
of the rays.

Yours faithfully, J. A. Tomkins.

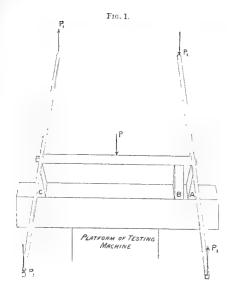


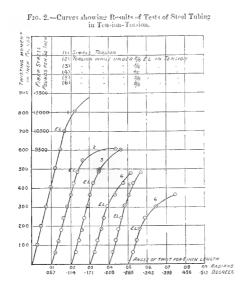


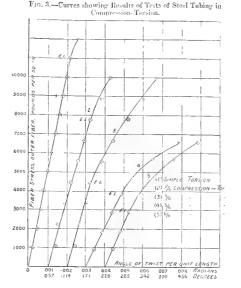


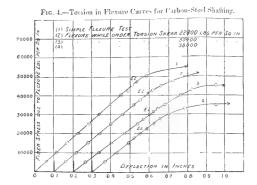


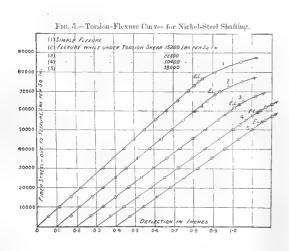












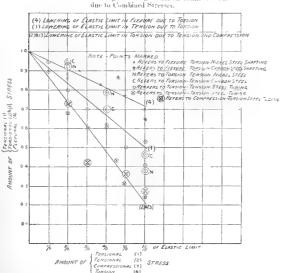
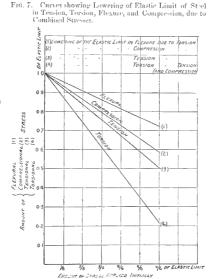
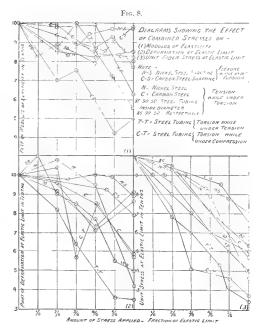


Fig. 6.—Curves showing Lowering of Elastic Limit of Steel

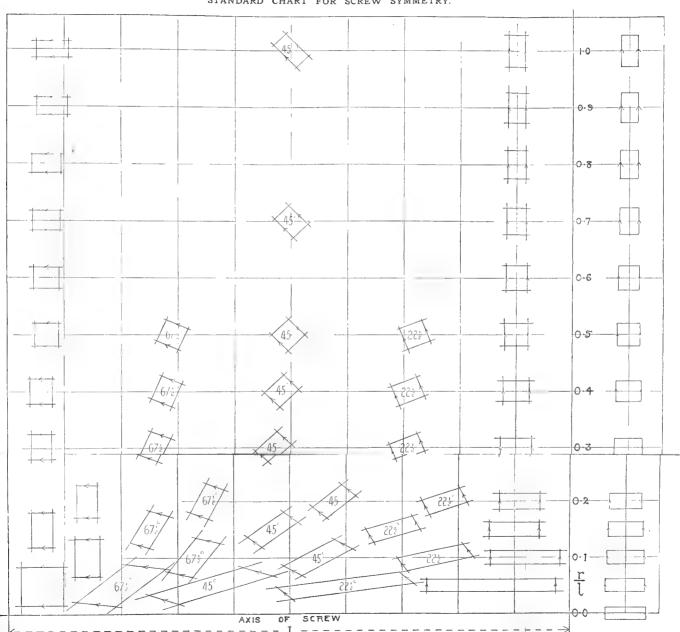




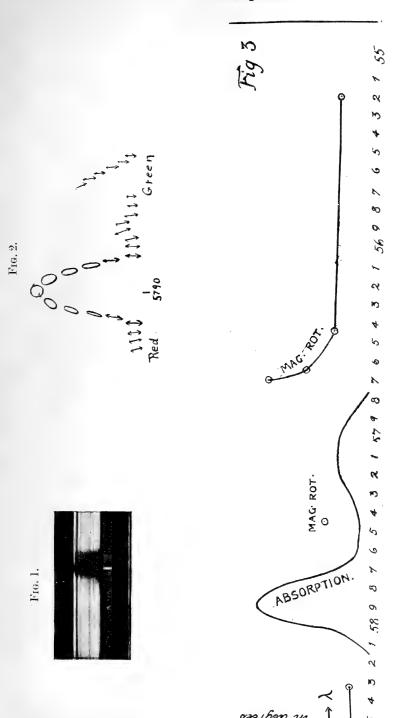




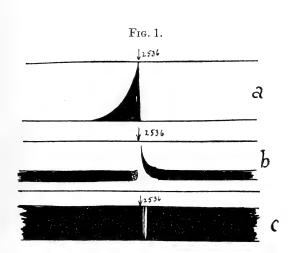


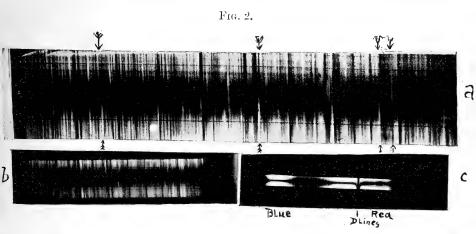














## LONDON, EDINBURGH, AND DUBLIN

## PHILOSOPHICAL MAGAZINE

AND

### JOURNAL OF SCIENCE.

[SIXTH SERIES.]

MARCH 1908.

XXIX. On the Practical Attainment of the Thermodynamic Scale of Temperature.—Part III. By J. Rose-Innes, M.A., B.Sc.\*

THE first part of this paper, which was published in the Philosophical Magazine some years ago, contained a method whereby the thermodynamic correction to a gasthermometer could be calculated from a knowledge of the Joule-Thomson effect for the gas, and of its isothermal compressibility at some one temperature (Phil. Mag. July 1901, pp. 131-133). The theory of the method given in that paper I still believe to be sound; but the accuracy of the final numerical results must depend not merely on the soundness of the theory followed, but also on the accuracy of the experimental data employed in the calculations. Several physicists have lately seen reason to entertain doubts concerning the trustworthiness of the measurements of the cooling-effect carried out by Joule and Kelvin. I have therefore thought it might be of some interest to develop a theory of the gas-thermometer in which less reliance is placed than formerly on the Joule-Thomson measurements. Not that we can afford to neglect the Joule-Thomson measurements altogether; every theory of the gas-thermometer is obliged to rely on them to some extent. But we are not obliged to go the length of accepting the absolute values of

<sup>\*</sup> Communicated by Prof. F. T. Trouton.

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the results obtained by Joule and Kelvin; we can form a consistent theory if we accept the Joule-Thomson figures as giving us simply the *relative* values of the cooling-effect for various temperatures and pressures of the streaming gas, and if we use these relative values in conjunction with other experimental data. Proceeding in this way, I have succeeded in diminishing some of the difficulties which were encountered in the first part of the paper.

Integration of the fundamental Differential Equation.

The differential equation for a gas streaming through a porous plug is

$$t\left(\frac{dv}{dt}\right)_p - v = JK \frac{\delta t}{\delta p}.$$

(See Kelvin's Reprinted Papers, vol. i. p. 248; see also

vol. iii. p. 179.)

The notion underlying the present plan is that in certain cases the Joule-Thomson measurements might be, as regards their absolute value, less trustworthy than observations made on some other physical quantity, and yet might be trusted to give us the relative values of the Joule-Thomson effect with sufficient accuracy; that is to say, the ratio of the values of the Joule-Thomson effect for two different sets of conditions might be given sufficiently well by means of the measurements. We may express this algebraically by supposing that the Joule-Thomson effect is equal to the experimentally determined value multiplied by  $\lambda$ , where  $\lambda$  is a constant factor, which must subsequently be either calculated or eliminated from the equations.

But even though complete confidence is not placed in the Joule-Thomson measurements as regards their absolute value, they may be supposed sufficiently accurate to tell us the

order of magnitude of  $JK \frac{\delta t}{\delta p}$ ; for such gases as are actually used for thermometric purposes  $JK \frac{\delta t}{\delta p}$  is always small, and will be treated as such in what follows. Further, the experiments of Joule and Kelvin show us that  $JK \frac{\delta t}{\delta p}$  may be treated as a function of the temperature only, if we are neglecting squares of small quantities.

Let us denote by the letter  $\nu$  the experimentally determined values of  $\frac{\delta t}{\delta p}$ ; then the above differential equation

may be written

$$t \binom{dv}{dt}_{\mathbf{r}} - v = JK \lambda v.$$

Divide by  $t^2$  and we have

$$\frac{1}{t} \left( \frac{dv}{dt} \right)_{p} - \frac{v}{t^{2}} = \frac{\text{JK } \lambda \nu}{t^{2}}.$$

Suppose that the suffixes 1 and 0 applied to v and t refer to the boiling and freezing points respectively; then let us integrate the last equation with regard to t from  $t_0$  to  $t_1$  at constant pressure p; we shall obtain

$$\frac{v_1}{t_1} - \frac{v_0}{t_0} = \lambda \int_{t_0}^{t_1} \frac{JK \nu}{t^2} dt = \lambda I \text{ (say)}.$$

Multiply by  $\frac{t_1}{v_0}$  and transpose; we obtain

$$\frac{v_1}{v_0} = \frac{t_1}{t_0} + \frac{t_1}{v_0} \, \lambda I.$$

Similarly by integrating at constant pressure p' we may obtain

$$\frac{v_1'}{v_0'} = \frac{t_1}{t_0} + \frac{t_1}{v_0'} \lambda I,$$

where dashed letters refer to the pressure p'. Subtracting and dividing by  $t_1-t_0$ , we have

$$\alpha' - \alpha = \frac{t_1}{t_1 - t_0} \left(\frac{1}{v_0'} - \frac{1}{v_0}\right) \lambda \mathbf{I},$$

where  $\alpha$  denotes the coefficient of expansion at constant pressure. Hence

$$\lambda = (\alpha' - \alpha) \div \left\{ \frac{t_1}{t_1 - t_0} \left( \frac{1}{v_0'} - \frac{1}{v_0} \right) \mathbf{I} \right\}.$$

If we calculate  $\lambda$  from this formula we shall be able to turn the numbers found by Joule and Kelvin into absolute values. We notice that a small percentage error in the value of  $\lambda$  will involve only the same percentage error in the finally accepted values for the Joule-Thomson effect,—itself a small quantity. Hence it is permissible to employ approximate methods to some extent in calculating  $\lambda$ . Thus we see that we require to know the values of  $t_0$  and  $t_1$ ; if we employ values for these quantities obtained from an uncorrected

hydrogen or nitrogen thermometer, we shall thereby introduce an error involving squares of small quantities into the finally accepted values of the Joule-Thomson effect: such an error may be safely disregarded. For much the same reason it is permissible to employ approximate methods in evaluating the integral I. We can effect the evaluation most conveniently by a graphical method,—plotting a suitable curve and finding its area by means of a planimeter in the usual way.

Having secured a sufficiently accurate value of  $\lambda$ , we may proceed to calculate the absolute values of the Joule-Thomson effect from the experimental results of Joule and Kelvin.

We will suppose that  $JK \frac{\delta t}{\delta \rho}$  throughout the field of observation may be fairly well reproduced by means of a series in descending powers of t, say  $\sum \frac{a_n}{t^n}$ , where n is either positive or zero. The fundamental differential equation may then be written

$$t\left(\frac{dv}{dt}\right)_p - v = \sum \frac{a_n}{t^n}.$$

Divide by  $t^2$ ,

$$\frac{1}{t} \left( \frac{dv}{dt} \right)_{p} - \frac{v}{t^{2}} = \sum \frac{a_{n}}{t^{n+2}}.$$

Integrate with respect to t along an isopiestic, and we obtain

$$\frac{v}{t} = P - \sum \frac{a_n}{(n+1)t^{n+1}},$$

where P is a function of p only. Multiply by pt, and we have

$$pv = pPt - p \sum \frac{a_n}{(n+1)t^n}.$$

The product pP is a function of p only and may be denoted by f(p); we thus have

$$pv = f(p) t - p \sum_{n=1}^{\infty} \frac{a_n}{(n+1) t^n}.$$

Denote pv by the single symbol  $\psi$ , and differentiate with respect to p, keeping t constant,

$$\left(\frac{d\psi}{dp}\right)_t = f'(p) t - \sum \frac{a_n}{(n+1)t^n}.$$

For several gases the quantity  $\left(\frac{d\psi}{dp}\right)_t$  is difficult to deter-

mine experimentally at temperatures where the Joule-Thomson effect has been measured; for such gases, however, it is always found possible to select some one isothermal as being fairly well determined; the temperature of this isothermal is never far removed from ordinary atmospheric

temperatures. The value of  $\left(\frac{d\psi}{dp}\right)_t$  along the selected isothermal is found in all cases to be independent of the pressure to the degree of accuracy to which we are at present working. It follows that

$$\frac{1}{t} \left\{ \begin{pmatrix} d\psi \\ dp \end{pmatrix}_t + \sum \frac{a_n}{(n+1) t^n} \right\}$$

must be constant along the selected isothermal; hence f'(p) will also be a constant along the same isothermal, say  $\epsilon$ . Further, the value of f'(p) from its form must remain unaltered for any isopiestic change; hence it will remain equal to  $\epsilon$  for any condition of the gas which can be reached from the above-mentioned isothermal by means of an isopiestic change. In other words, f'(p) must be equal to the constant  $\epsilon$  to our present degree of accuracy.

Since  $f'(p) = \epsilon$ , it follows that

$$f(p) = \mathbf{R} + \epsilon p,$$

where R is an arbitrary constant introduced by the integration. Employing this value of f(p) we obtain

$$\psi = \mathrm{R}t + \epsilon \, pt - p \, \Sigma \, \frac{a_n}{(n+1) \, t^n}.$$

If v is kept constant while p and t are both made to increase together, the term  $\epsilon pt$  will ultimately become more important than Rt. As it seems improbable that this can represent the true state of things at high temperatures we ought to try to make  $\epsilon$  vanish. We can secure this result if we can put

$$\left(\frac{d\psi}{dp}\right)_{t} = -\sum \frac{a_{n}}{(n+1)t^{n}}$$

along the isothermal we have selected for measuring the deviation from Boyle's law. Choosing the series  $\sum \frac{a_n}{t^n}$  so as to

306 Mr. J. Rose-Innes on the Practical Attainment of fulfil the last condition, we obtain the characteristic equation

$$\psi = \operatorname{R} t - p \sum_{n=1}^{\infty} \frac{a_n}{(n+1) t^n}.$$

We shall next enquire what is the change in the coefficient of expansion corresponding to the above equation. We have

$$v_0 = \frac{Rt_0}{p} - \sum \frac{a_n}{(n+1)t_0^{n}},$$

$$v_1 = \frac{Rt_1}{p} - \sum \frac{a_n}{(n+1)t_1^{n}}.$$

Multiply the last equation by  $\frac{1}{v_0}$ , the last but one by  $\frac{t_1}{v_0 t_0}$ , and subtract, we obtain

$$\frac{v_1}{v_0} - \frac{t_1}{t_0} = \frac{1}{v_0} \left\{ \frac{t_1}{t_0} \sum \frac{a_n}{(n+1) \ t_0^n} - \sum \frac{a_n}{(n+1) \ t_1^n} \right\}.$$

Similarly for pressure p' we should have

$$\frac{{v_1}'}{{v_0}'} - \frac{t_1}{t_0} = \frac{1}{{v_0}'} \left\{ \frac{t_1}{t_0} \Sigma \frac{a_n}{(n+1) \, {t_0}^n} - \Sigma \frac{a_n}{(n+1) \, {t_1}^n} \right\}.$$

These last two equations after a little reduction yield

$$\alpha' - \alpha = \left(\frac{1}{v_0'} - \frac{1}{v_0}\right) \frac{t_1}{t_1 - t_0} \left\{ \sum \frac{a_n}{(n+1) t_0^{n+1}} - \sum \frac{a_n}{(n+1) t_1^{n+1}} \right\}.$$

We see then that the series  $\sum \frac{a_n}{t^n}$  must be chosen so as to satisfy three conditions:—(i.) The observed Joule-Thomson effect at different temperatures must be proportional to the values of the expression  $\sum \frac{a_n}{t^n}$ ; (ii.) the value of  $\left(\frac{d\Psi}{dp}\right)_t$  must be represented by  $-\sum \frac{a_n}{(n+1)t^n}$  for some single isothermal; (iii.) the observed change in the coefficient of expansion must agree with the calculated value.

#### Variation of the above Method.

In the investigation given above I have assumed that observations of the Joule-Thomson effect had been made at a sufficient number of different temperatures to fix fairly

definitely the form of the curve  $\frac{JK\nu}{t^2}$  plotted against t between the limits  $t_0$  and  $t_1$ . It may happen, however, that the observations are not sufficient in number to fix the curve with as much definiteness as could be desired, and in such a case the resulting uncertainty in the value of I may lead to errors in the calculated Joule-Thomson effect too large to be fairly comparable with the squares of small quantities. In order to avoid errors from such a cause the most convenient plan is to take some account of the observed value of  $\left(\frac{d\psi}{dp}\right)_t$  in settling the form of the curve. This plan may be carried out in substance by means of the following device:—

Suppose we find a series in descending powers of t, say  $\sum \frac{c_n}{t^n}$ —where n is either positive or zero—such that  $\sum \frac{c_n}{t^n}$  is equal to the observed Joule-Thomson effect, and  $-\sum \frac{c_n}{(n+1)t^n}$ is equal to the observed value of  $\left(\frac{d\psi}{d\rho}\right)_t$  along the selected isothermal. Thus  $\sum \frac{c_n}{t^n}$  is an approximation to the series we are seeking, but it needs correction. Let us find a second series in descending powers of t, say  $\sum_{i}^{e_n}$ —where n is either positive or zero—such that  $\sum_{i=1}^{n} \frac{e_{i}}{r^{n}}$  is equal to the observed Joule-Thomson effect, and  $\sum \frac{e_n}{(n+1)t^n}$  is zero along the selected isothermal. Then the series  $\sum_{n=0}^{\infty} \frac{c_n + \kappa e_n}{\epsilon^n}$ , where  $\kappa$  is a constant at our disposal, is equal to  $1+\kappa$  times the observed Joule-Thomson effect, while  $-\sum \frac{c_n + \kappa e_n}{(n+1) t^n}$  is equal to the observed value of  $\left(\frac{d\psi}{dp}\right)_t$  along the selected isothermal. Hence the series  $\sum \frac{c_n + \kappa e_n}{t^n}$  fulfils the first two of the conditions mentioned above, and we can make it fulfil the third by properly choosing  $\kappa$ . In fact, when we employ this new series, we find that the difference between the coefficients of 308 Mr. J. Rose-Innes on the Practical Attainment of expansion at constant pressures p and p' is given by

$$\begin{split} a' - \alpha &= \frac{t_1}{t_1 - t_0} \bigg( \frac{1}{v_0'} - \frac{1}{v_0} \bigg) \bigg\{ \sum \frac{c_n}{n+1} \bigg( \frac{1}{t_0^{n+1}} - \frac{1}{t_1^{n+1}} \bigg) \\ &+ \kappa \sum \frac{e_n}{n+1} \bigg( \frac{1}{t_0^{n+1}} - \frac{1}{t_1^{n+1}} \bigg) \bigg\} \,. \end{split}$$

This equation may be considered as fixing the value of  $\kappa$ ; once  $\kappa$  is known we know also the series  $\sum \frac{c_n + \kappa e_n}{t^n}$ , which fulfils the three conditions laid down at the end of last section. It is clear that  $1 + \kappa$  is equivalent to the  $\lambda$  of last section.

Application of the above Theory to Hydrogen and to Nitrogen.

We have next to consider the application of the above theory to the gases actually used for thermometric purposes. It is found that for hydrogen and for nitrogen we can fulfil the three conditions, specified at the end of the first section, with sufficient accuracy by putting

$$\sum \frac{\alpha_n}{t^n} = \alpha_0 + \frac{\alpha_1}{t} + \frac{\alpha_2}{t^2}.$$

It is worth remarking that the precise algebraic form which we choose for the series does not perceptibly affect the final numerical results for the thermodynamic corrections, so long as we employ the same experimental data to calculate the constants, and so long as we keep within the limits of temperature and pressure over which the Joule-Thomson effect has been observed. We may express this by saying that the three conditions determine the thermodynamic corrections with arithmetical uniqueness within the field of observation over which they hold good. Hence, if we do not attempt to extrapolate, we may choose the form of our series solely with a view to ease in arithmetical calculation, and the form suggested above is on the whole the most convenient for such a purpose.

The experimental data relating to hydrogen and to nitrogen

will be considered separately.

Hydrogen—This gas was subjected to the porous-plug experiment by Joule and Kelvin; the results are given in Kelvin's Reprinted Papers, vol. iii. p. 175. There was a heating effect which amounted, per 100 inches of mercury

of differential pressure, to  $0^{\circ}\cdot 100$  C. at temperatures of  $4^{\circ}$  C. or  $5^{\circ}$  C., and to  $0^{\circ}\cdot 155$  C. at temperatures of from  $89^{\circ}$  C. to  $93^{\circ}$  C. The change of  $\alpha$  with the pressure was examined by M. Amagat (see Annales de Chimie et de Physique,  $6^{\circ}$  série, t. xxix. p. 127); it is unfortunate that his experiments apply to high pressures only, but since the value of  $\alpha$  appears to vary steadily with the pressure over a considerable range of pressure, we may probably make use of his results without introducing any sensible error. The decrease in  $\alpha$  corresponding to an increase of 100 atmospheres pressure is

·00018. The value of  $\left(\frac{d\boldsymbol{\psi}}{dp}\right)_t$  can also be obtained from

M. Amagat's experiments (see his paper, Ann. de Chimie et de Physique,  $5^{\rm e}$  série, vol. xxii.). In the first part of the present paper I practically accepted M. Amagat's statement that the isothermals of hydrogen,— $\psi$  plotted against p—form a set of parallel straight lines with a slope correspond-

ing to  $\left(\frac{d\psi}{dp}\right)_t = 00078$ . Though M. Amagat warns his readers that this law is only approximate, I came to the conclusion that it was sufficiently accurate for the purpose I

had in view; accordingly I took  $\left(\frac{d\boldsymbol{\psi}}{dp}\right)_t$  to be .00078, and

attached this value to the temperature 50° C. as being midway between the boiling- and freezing-points. But a more careful examination of M. Amagat's results has shown me that the rough method I employed was somewhat rougher than I supposed. The curvature of the isothermals—though not very apparent to the eve in a diagram—indicates a smaller deviation from Boyle's law for those portions of the isothermal which are nearer the axis of zero pressure; and I find that the isothermal for 17°.7 C. yields a value of

 $\left(\frac{d\psi}{dp}\right)_t = 000645$  at low pressures. This value agrees very

nearly with that given by MM. Leduc & Sacerdote, viz. '00064 at 16° C. (see Comptes Rendus, t. exxv. 1897, p. 299), and is not far removed from the value given by Prof. K. Onnes, viz. '000623 at 20° C. (Schalwijk, Académie des Sciences d'Amsterdam, June 1901).

Nitrogen.—The isothermal compressibility of this gas has been studied by M. Amagat (Comptes Rendus, t. xcix. p. 1153); the gas was subjected to the porous-plug experiment by Joule & Kelvin (Kelvin's Reprinted Papers, vol. i. p. 421); and the coefficient of expansion at various constant pressures

has been determined by M. Chappuis (Trav. et Mém. du Bur.

Int. xiii. pp. 21-25).

The experiments of M. Amagat on the compressibility of nitrogen were conducted chiefly at high pressures; but there is one measurement of pv at atmospheric pressure on the isothermal of  $16^{\circ}$  C., so that we may obtain the desired

value of  $\left(\frac{d\psi}{dp}\right)_t$  at this temperature by means of an interpolation. In the earlier part of this paper I gave -0.00035 as the value founded on M. Amagat's experiments: and this figure is very nearly in accord with that subsequently found by Lord Rayleigh from his own experiments, viz., -0.00034 (Proc. Roy. Soc. lxxiii. no. 490, p. 153). The small difference between these two estimates is not sufficient to cause any appreciable change in the final numerical results, so that I have simply retained my former value of

 $\left(\frac{d\psi}{dp}\right)_t$ .

M. Chappuis's most trustworthy determinations of the coefficient of expansion were made with a thermometer having a reservoir of iridio-platinum. His observations with this instrument may be divided into two groups: the first group having a mean pressure of 1.001855 m. of mercury gave a value of the coefficient 0.00367315, the second group having a mean pressure of 1.386787 m. of mercury gave a value of the coefficient 0.00367775.

The value of the Joule-Thomson effect was determined by Joule & Kelvin for three initial temperatures, viz.: 7°-204 C., 91°.415 C., and 91°.965 C. These last two temperatures are so close that we should not expect to find any marked difference in the Joule-Thomson effect as we pass from one to the other; and, as a matter of fact, the cooling-effect per 100 inches of mercury, for the actual gas employed, is much the same in both cases. But the figures which are given for the Joule-Thomson effect of pure nitrogen, as the result of an extrapolation, differ considerably in the two cases; so much so that it is clear the difference cannot be due to the small change in the initial temperature, but that we are in presence of a serious experimental error. I have, as in the earlier part of this paper, altogether rejected the value at 91°.965 °C. on the ground that the experimental gas in this case contained a large percentage of oxygen, and that the figure given for pure nitrogen is the result of a considerable extrapolation.

Making use of the data referred to above, we obtain the following values for the constants  $a_0$ ,  $a_1$ ,  $a_2$ :—

	Hydrogen.		Nitrogen.
$a_0$	 00060654	$\nabla_0$	$0018319 \text{ V}_{0}$
$a_1$	 —·17378 V₀		$1.0105  \mathrm{V_0}$
$a_2$	 65.754 Vo		108·73 V₀•

Here  $V_0$  is the volume of 1 gramme of the gas at standard temperature and pressure.

Thermodynamic correction to the Gas-Thermometer.

In the earlier part of this paper I considered the thermodynamic correction to the gas-thermometer on the assumption that the Joule-Thomson effect could be reproduced with sufficient accuracy by an expression of the form

$$a_0 + \frac{a_1}{t} + \frac{a_2}{t^2}$$
.

The algebraic work there given is still applicable, since I propose to adhere to the same algebraic formula for the Joule-Thomson effect, though with altered values of the constants.

Hydrogen.—The coefficient of increase of pressure at constant volume has been carefully investigated by M. Chappuis. His measurements are probably the best that have yet been published; unfortunately, owing to experimental difficulties, there is still an appreciable discordance between several of his determinations. As the result of his experiments conducted at three different times, he gives the following numbers for the coefficient:—

·00366254 with initial pressure 998.9 mm. of mercury.

Of the three determinations here given the two first were made with a reservoir of iridio-platinum, and the third with a reservoir of hard glass. The variations in the value of the initial pressure are small and may be disregarded for our present purpose. I am inclined to place the greatest reliance on the last determination, which was made with a reservoir of hard glass; since M. Chappuis himself, in another publication, refers to the inconvenience caused by the permeability of metals to hydrogen at high temperatures, and it is quite

possible that even at lower temperatures some slight interaction may take place between the walls of a metal vessel and the enclosed gas ("L'échelle thermométrique normale et les échelles pratiques," pp. 3–4). For these reasons I prefer to take the figure '00366217 as the most probable value for the coefficient of the increase of pressure at constant volume; we thus obtain 273·062 as the "uncorrected estimate" of the freezing-point of water. By employing the values of the constants given at the end of last Section, we may readily calculate that the proper correction to be applied is 0°·069, so that we obtain 273°·131 as the estimate of the freezing-point.

The thermodynamic corrections to the readings of the hydrogen thermometer are given in the following Table:—

TABLE 1.								
	Corre	ction.		Correction.				
Temp.	Constant pressure thermometer.	Constant volume thermometer.	Temp.	Constant pressure thermometer.	Constant volume thermometer.			
		1						
0° C.	0	0	60° C.	0023	<b>-</b> ·0015			
10	0011	0007	70	0019	0013			
20	0018	- 0012	80	0014	0010			
30	- 0023	0015	90	0008	0005			
40	- 0025	0016	100	0	0			
50	0025	0016						
1	1							

TABLE I.

The constant-pressure thermometer is supposed to be under the pressure of 1 atmosphere, and the constant-volume thermometer is supposed to be under the pressure of 1 atmosphere at the freezing-point.

Nitrogen.—We saw that M. Chappuis's value for the coefficient of expansion at a constant pressure of 1.002 m. was .00367315; from this figure we obtain 272.246 as the "uncorrected estimate" of the freezing-point of water. We may employ the values of the constants given at the end of last Section to calculate the necessary correction: we easily find that it is equal to 0°890. Hence we obtain 273.136 as the "corrected estimate" of the freezing-point.

The following Table gives the thermodynamic corrections for the constant-pressure thermometer under 1 atmosphere pressure, and for the constant-volume thermometer having the pressure of 1 atmosphere at the freezing-point:—

TABLE II.

	Corre	ction.		Correction.		
Temp.	Constant pressure thermometer.	Constant volume thermometer.	Temp.	Constant pressure volum thermometer.		
0° C.	0	0	60° C.	0163	- 0026	
10	- 0074	0011	70	0138	0022	
20	0126	0019	80	0102	0016	
30	0159	0025	. 90	0056	0009	
40	-0175	0027	100	. 0	0	
50	- 0176	0028				

On the Applicability of the foregoing Theory to actual Gas-Thermometers.

The numerical results given in the tables of last Section show that the thermodynamic corrections to the constant-volume thermometer are small quantities, when we employ hydrogen or nitrogen at standard density; and it becomes of importance to examine what sort of relation these corrections bear to the mistakes of reading due to the unavoidable errors of experiment. It has been already remarked that in the case of hydrogen the nature of the walls of the containing vessel appears to exert a perceptible influence upon the pressure of the gws. Great interest therefore attaches to a careful comparison, carried out by M. Chappuis, between the readings of two hydrogen thermometers, both used at constant-volume, but differing in the material of their bulbs. The following figures were obtained:—

TABLE III.

Temperature.	Excess of reading of mercury-in-glass thermometer over constant-volume hydrogen thermometer with:				
	Glass reservoir.	Metai reservoir.			
10° C.	.051	.052			
20	.076	·085			
30	.095	•102			
40	·108	107			

(Trav. et Mém. du Bur. Int. xiii. p. 39). The pressure at

freezing-point of the hydrogen thermometers was in both

cases 1 metre of mercury.

An inspection of the above Table shows us that the difference of reading between two hydrogen thermometers is quite appreciable; it is as high as 0°.009 C., for instance, at 20° C. Hence, at this temperature, one at least of the two thermometers must be wrong in its reading by a fairly large figure in the third place of decimals. This suggests that even where the two thermometers agree, as in the neighbourhood of 40° C., we cannot be certain there is no error: it is just as likely that both thermometers happen to exhibit at this place the same divergence from the thermodynamic scale, the divergence being of the same order of magnitude as that actually proved to exist at 20° C.

We readily find from the tables of last Section that the

We readily find from the tables of last Section that the thermodynamic correction at 20° C. for the hydrogen thermometer, under the conditions of pressure observed by M. Chappuis, is less than 0° 002 C. Such a quantity is considerably smaller than the error proved to exist in at least one of the two hydrogen thermometers. A similar remark applies to the thermodynamic correction at 30° C.; and it is quite likely, though not actually proved, that the correction is smaller than the experimental error at other temperatures between the freezing- and boiling-points. Hence the thermodynamic corrections to the readings of a constant-volume

hydrogen thermometer are usually neglected.

As the standard instrument for thermometric purposes it is usual to take just such an instrument as those examined by M. Chappuis, viz., a constant-volume hydrogen thermometer with a pressure of 1 metre of mercury at the freezingpoint. But since we do not really know which of his two thermometers is the more correct in its indications, we may inadvertently have let our choice fall upon the more faulty one for the standard instrument. Hence we cannot trust our standard thermometer in the third place of decimals for anything more than thermoscopic purposes. And since the difference of reading of the two hydrogen thermometers at 20° C. is greater than the thermodynamic correction to the constant-volume nitrogen thermometer at the same temperature, we cannot be certain that the usual standard thermometer is everywhere superior in the accuracy of its actual readings, to the constant-volume nitrogen thermometer.

#### Conclusion.

We have found that there is a good agreement between the two estimates of the freezing-point which are given in the present part of this paper, and are derived from the experimental data concerning hydrogen and nitrogen respectively; the closeness of this agreement entitles us to consider the present method as superior in accuracy to those previously employed. We may also place considerable confidence in the tables of thermodynamic corrections given in this paper; because, as has been already pointed out, while we confine ourselves within the limits of temperature and pressure, within which the Joule-Thomson effect has been observed, the precise algebraic form of the expression chosen to represent the effect has practically no influence on the final numerical results. But outside these limits the algebraic form of the expression chosen to represent the Joule-Thomson effect may, and in general will, exercise considerable influence on the final numerical results. For this reason I have not given the thermodynamic correction for temperatures lying either below the freezing-point or above the boiling-point. And until we know the true form which ought to be employed for the Joule-Thomson effect, the results of calculating the thermodynamic corrections for such temperatures must be largely speculative.

The above considerations point to a large gap in our knowledge, and some physicists have endeavoured to meet the difficulty by employing a rational formula for the Joule-Thomson effect based upon some molecular hypothesis regarding the constitution of gases. The drawback to such a method of procedure is that the trustworthiness of the final numerical results is made to depend not merely on the two laws of Thermodynamics and on data derived from experiment, but also on the truth or falsehood of a speculative hypothesis. The introduction of such speculations into the treatment of a purely thermodynamic question must be considered as being to a large extent a step backwards. On the other hand, it is not possible to remain contented with the present state of our knowledge of the thermodynamic correction to a gas-thermometer; we have to confine our theory to temperatures which lie between the boiling- and freezing-points, or which are but slightly removed from

those limits.

The most simple and at the same time the most effective method of meeting the difficulty would be to repeat the Joule-Thomson experiments over a much wider range of

temperature. If an empirical formula were found to fit the values of the Joule-Thomson effect over a wide range of temperature, then we might very well conclude—apart from any molecular hypothesis—that this formula was the proper one to employ. It is true that measurements of the Joule-Thomson effect are far from easy to carry out satisfactorily; still, the difficulties are not insuperable, and there is no reason why the success of Joule and Kelvin in this line should not be repeated. The measurements of these last-named experimenters appear to have been confined within narrow limits of temperature, not so much because observations were impossible at temperatures outside these limits, as because Lord Kelvin imagined he had already discovered the true formula for the Joule-Thomson effect.

The plan here advocated of repeating the Joule-Thomson experiments over a wider range of temperature is all the more feasible since we have shown that we require only the relative values of the Joule-Thomson effect. source of error which multiplies all the Joule-Thomson effects by the same factor would be eliminated. The errors of experiment which give rise to ordinary "wobbling" would also be eliminated by the present method. Indeed, the only sources of error which are liable to affect the final numerical results to a sensible degree are those which tend persistently to increase or diminish the Joule-Thomson effect at higher temperatures as compared with that at lower. Provided that such sources of error were either abolished or properly allowed for, we could place considerable confidence in the final numerical results, and probably succeed in throwing great light on a fundamental problem of thermodynamics.

As appears from my paper, my object has been to find a purely phenomenological method of calculating electromagnetic effects, which should harmonize with all the facts

XXX. On the Principle of Relativity and on the Electromagnetic Mass of the Electron. A Reply to Mr. E. Cunningham. By A. H. BUCHERER, D.Sc., Professor in the Bonn University\*.

IN the October number of this Magazine Mr. E. Cunningham raises some objections to the theory of relativity as defined by me in the April number. I wish to say a few words in reply in order to show that Mr. Cunningham's remarks are due to a misconception on his part of the real meaning and bearing of the principle as used by me.

<sup>\*</sup> Communicated by the Author.

of observation, leaving it to future endeavours to find a physical interpretation of this method. No doubt this way of proceeding implies a certain resignation. But in view of the failure of the electromagnetic theories advanced as yet, it seems the safest road to follow.

My method rests on the following principles and de-

finitions:—

(1) The validity of the Maxwellian "differential" equations

associated with ordinary kinematics.

(2) The distinction, for the mere sake of calculation, between active and passive systems, whenever forces are concerned which two electromagnetic systems in uniform relative motion exert on each other.

(3) The prescription: Whenever the force on one of the two systems due to the other is required, choose the former as the passive one and calculate the force on it exactly as in the original Maxwellian theory, as though it were "at rest in the æther" and the other "moving through the æther."

I have proved (l. c.) that this prescription is consistent, i. e. that the forces thus calculated are identical whichever of the two systems is chosen as passive. This implies the prin-

ciple of relativity of motion for the systems considered.

Mr. Cunningham will admit that this method of calculating is perfectly definite, and by a careful comparison with the Lorentz-Einstein principle he will convince himself that the two principles are essentially different. The remark of Mr. Cunningham that my principle is identical with that of Einstein except that I omit the transformation of time and space coordinates, appears untenable also from the following consideration. Evidently, according to Mr. Cunningham, a transformation of the forces experienced by a moving electron in a condenser field and in the field of an electromagnet as calculated by me (l. c.) should yield the expressions given by Einstein and Lorentz. But an inspection of my equations proves the impossibility of such a transformation. In fact no other known theory of electromagnetism leads to these forces.

As I employ the ordinary kinematics, only a spherical electron will fit in my theory. Mr. Cunningham has overlooked this circumstance.

However, it does not follow that the same formula as Abraham's should be applied, as this formula is connected with the expression of the field energy, and the latter is introduced by me as a special hypothesis (l. c. p. 418).

Whereas it will be impossible to point to any discrepancy Phil, Mag. S. 6. Vol. 15. No. 87. March 1908.

between my theory and experimental facts in the electrodynamics of the relative uniform motion of electric and magnetic masses, the Lorentz theory finds unsurmountable difficulties on theoretical grounds. As was first conclusively shown by Abraham, the Lorentz deformation excludes a purely electromagnetic basis of mechanics. The work of the external electric forces acting on the electron does not have its exact equivalent in the increase of the electromagnetic energy of the electron. Therefore a certain inner energy of non-electromagnetic character must be ascribed to the electron. The same conclusion must be drawn from Mr. Cunningham's calculations, if they are properly interpreted.

Mr. Cunningham says the Lorentz-Einstein theory is the only theory that can account for certain optical phenomena. In fact, he asserts that it is required "to explain how a light-wave travelling outwards in all directions with velocity C relative to an observer A may at the same time be travelling outwards in all directions with the same velocity relative to an observer B moving relative to A with velocity v." Mr. Cunningham then proceeds to show that this requirement is satisfied by the Lorentz-Einstein transformation.

I am not aware that such a "requirement" is necessary to explain any known fact of observation.

# XXXI. On the Factors serving to determine the Direction of Sound. By T. J. BOWLKER\*.

In the summer of 1906, while on a steamship off the coast of Maine, U.S.A., I was roused about midnight by the blowing of foghorns, and presently followed the shock and grinding of a collision. It appeared to me that the accident could only be explained by a mistake in judging of the direction of the foghorns of the colliding vessels. This accident suggested a study of the factors determining the direction

from which sound appears to come.

During the winter of 1906-1907 I made some experiments. In one of them I placed the ends of two rubber tubes of equal lengths at the ears and moved the end of one towards or away from the source of sound. With equal lengths of tube I thought that the friction and resonance effects would be the same. The sound, as heard through the tubes, did appear to move somewhat to one side or other of the head, but the movements did not appear to have any relation to the wave-length, and the movements were very irregular.

<sup>\*</sup> Communicated by the Author.

I realized how hopeless it was to try such experiments in a small laboratory where perhaps 90 per cent. or more of the sound had already suffered one or more reflexions; the experiment merely suggested a possible method of studying the position of nodes and antinodes in such a closed space.

Later an apparatus to determine the direction of sound by magnifying the intensity effects by means of two sound-receivers on opposite sides of a large flat board was surprisingly inadequate except in the case of the higher notes, and led to the conclusion that it was very probable that phase had a good deal to do with our judgment of the direction of sound.

I postponed further experiments on the direction of sound until the summer of 1907, when I should have an opportunity

of trying them in the open air.

In the meantime I saw Lord Rayleigh's paper in the Philosophical Magazine proving conclusively, in an ingenious manner in the laboratory, that phase in some cases gave a sense of direction. It only remained to show to what extent and within what limits these effects were produced. In June 1907 therefore I proceeded to try experiments in the open air, the apparatus being a set of adjustable organ-pipes, made for me by Hutchings & Votey of Cambridge, Mass., and cylindrical tubes of various lengths applied to the ears.

The tubes were of sheet aluminium, and they could have their length altered by sliding one within another.  $2\frac{1}{4}$  inches was chosen as the diameter, because then the tube could be readily fitted quite closely round its whole circumference

against the head.

The source of sound was placed at a distance of about 30 feet from the observer in an open field. It was at once found that with two unequal tubes applied to the ears, and with the observer facing the source of sound, the source appeared to move to the opposite side to that on which the longer tube was applied. (This, as will be seen later, is only

true within certain limits.)

After certain preliminary experiments, the ground was pegged out in an arc of a circle  $28\frac{1}{2}$  feet in radius. The source of sound was placed at a point of this arc, and pegs were placed at intervals of  $4^{\circ}$  along the circumference up to  $60^{\circ}$  on each side of the source. The observer was situated at the centre of the circle. As the image of the source moved the observer continually faced the image and noted its apparent position on the arc. This position could be fixed with an error of not more than one or two degrees.

Z 2

Some of the results obtained are given in the table below. In order to avoid psychological errors of imagination and expectation, no guesses at what would happen were made, nor any theory formed as to the probable position of the image until two or three complete sets of experiments had been made. It was found, however, that after a little practice the location of the image could usually be obtained with such certainty that these precautions were unnecessary.

In the following tables r. indicates that the tube was over the right ear or that the movement of the sound-image was

to the right, whilst l. indicates the same for the left.

L is the length from the extremity of one tube to the extremity of the other when both are applied to the head.

 $\theta$  is the angular displacement of the image when the longer

tube is nearer the source.

 $\theta'$  is the angular displacement when the shorter tube is nearer the source.

Note of Wave-length = 19 inches.

Length of tubes over ears.	Diff. of length of ear-tubes=D.	Displacement of image $= \theta$ .	$     \begin{array}{c}       \text{L sin } \theta. \\       \theta = \text{angle to} \\       \text{the left.}     \end{array} $	L sin $\theta'$ + D. $\theta'$ = angle to the right.
Inches.	Inches.		Inches.	Inches.
7 over r. 6 over	1	2° l.	.6	
8 r. 6 l	2	6° 1.	2.1	
9 r. 6 l.	3	8° 1.	2.9	
10 r. 6 l. }	4	10° l.	3.7	
12 r. 6 l. \	6	16° l.	6.7	
$\begin{bmatrix} 14 \text{ r.} \\ 6 \text{ l.} \end{bmatrix}$	8	10° 1.	4.1	
$\left\{\begin{array}{c} 15\frac{1}{2} \text{ r.} \\ 6 \text{ l.} \end{array}\right\} \dots$	$9\frac{1}{2}$	$\begin{cases} 20^{\circ} \text{ l. and} \\ 20^{\circ} \text{ r. & 0}^{\circ} \end{cases}$	9.2	18.7
$\begin{bmatrix} 18 \text{ r.} \\ 6 \text{ l.} \end{bmatrix}$	12	$\left\{ egin{array}{ll} 24 ^{\circ} \mathrm{l.} \ 8 ^{\circ} \mathrm{r.} \end{array}  ight.$	12.3	16.2
19 r. 6 l. }	13	{ 26° l. 6° r.	13.6	16·1

Now if an image, apparently in front, is produced when the phases arriving at the ear are in agreement, L sin  $\theta$  should be equal to the difference of length of the ear-tubes, and L sin  $\theta' + D$  should be approximately equal to the wavelength. We find that this is the case. There are, however, some anomalies, notably when the angle suddenly changes from 16°l. with a tube 12 inches long over the right ear to

10° l. when the tube is made 14 inches long. This is doubtless due to resonance in the 14-inch tube increasing the intensity at the right ear. Subsequent experiments confirmed this view. In later experiments large loose wads of cottonwool were inserted at the outer ends of the tubes. This proves a very effective means of checking resonance, whilst not interfering very much with the intensity. In this manner, using sounds of various wave-lengths, it was proved that an image appeared in front of the observer when the phases of the waves arriving at the ears were approximately in agreement. A better arrangement was devised, however, later, and an account of these later experiments appears further on.

The next point was to determine, to what extent the image of the source was displaced whilst the observer continually faced the source, and how this displacement depended on the wave-length. For this purpose two tubes were taken, and the observer continually faced the source and tried to note the direction in which the image appeared: in some cases only one tube was applied to the ear.

One example is given below.

Note of Wave-length 26.8 inches.

Length of tube placed over one ear—the other ear free.	Angular dis- placement of sound-image with tube over the right ear.	placement of sound-image with tube over	tubes	gths of splaced er the ears.	Angular displacement with the longer tube over the right ear.	Angular displace- ment with the longer tube over the left ear.
Inches.			Tn	ches.		
4	4° 1.	2° r.	9	& 6	16° 1.	4° r.
6	8° 1.	4° r.	12	& 6	28° 1.	8° r.
8	20° 1.	10° r.				
9	24° l.	16° r.	15	& 6	40° l.	14° r.
12	36° l.	24° r.	17	& 6	60° 1. & 60° r.	20° r.
15	40° l. & 46° r.	30° r. & 30° l.	19	& 6	30° r.	45° r.
17	40° r.	40° r. & 40° l.	$23\frac{1}{2}$	& 6	12° r.	30° r.
18	30° r.	30° 1.	1		r	(2) 00 p &
19	20° r.	24° l.	25	& 6	4° r. {	(?) 0° r. & (?) 0° l.
20	10° r.	16° l.			·	(.) 0 1.
21	00	8° l.				
22	00	0	28	& 6	4° r.	(?) 0° l.
24	4° l.	0	28	& 4	4º 1.	0
26	10° l.	4° r.				
$27\frac{1}{2}$	20° 1.	8° r.				

It would appear from the above that the image crosses over from left to right, or from right to left, when there is a difference of about half a wave-length in the arrival of the sound at the two ears—the image being on that side at which the sound-wave arrives first.

It will be noted that in the earlier stages a displacement was more readily produced when the phase was advanced on the left ear. I was thus asymmetric with regard to my hearing, and I have found the same to be true of others.

I also found that the hearing mechanism connected with the formation of the position of the image is capable of fatigue. After listening intently for some time with one ear towards the source, the position of the image does not return to exactly the same place as before. I tried to determine whether fatigue for one note resulted in a lessened displacement of the sound-image of another note, but I was unable to settle this point. These phenomena may be of interest to

the experimental psychologist.

Similar experiments were tried with notes of other wavelengths, the result always indicating that there was a sudden appearance of an image on the other side of the field of sound-view when the difference of phase at the two ears was approximately half a wave-length. The maximum angle of displacement increased up to 90° as the wave-length of the sound increased; a wave-length of about 36 inches being the first that gave an image displaced 90°. Sounds with longer wavelength gave a displacement of 90° before a phase-difference of half a wave-length was reached, and the sound-image then seemed to spread over a continually increasing length of arc on each side of 90°.

It is hard to determine the actual position of a sound-image when the observer is facing the source, and the sound-image is displaced through a large angle. Up to 20° I think I can tell the position to within 2°, from 20° to 30° to within 4°, from 30° to 40° to within 6°, from 40° to 50° to within 8°, after 55° I may be 10° or more out. When possible I find it best to point with the arm outstretched in the direction from which the sound appears to come, but when holding two tubes to the ears one cannot do this.

In the above experiments resonance effects were still rather disturbing, and, as the general behaviour of the soundinages had been ascertained, a new arrangement was introduced.

In this the ear-tubes were of equal length, and a rightangled bend was inserted in each, so that the outer portions of the tubes were approximately vertical. The plane through the outer edges of these tubes was horizontal. With this arrangement the resonance was the same in both tubes, and the intensity was also the same for both.

The distance apart of the centres of the tubes was 31 inches, and their diameter was 2 inches. The tubes were luted into

the right-angled bend with stiff modelling-clay.

With this arrangement, when facing the source, the image did not always coincide exactly with the source, perhaps owing to the tubes being slightly unsymmetrical with regard to the head when closely pressed against it to make a tight

joint at the junction of head and tube.

The method of procedure was—first to find the true zero by applying the ear-tubes and facing the source, then turning the head until the image appeared to be straight in front and then noting the reading. (The error here would probably not be more than 1°.) Then the head was turned slowly to the left, this caused the image to move more or less to the right, at a certain position in the rotation of the head an image appeared suddenly to the left—this new image made an angle with the symmetric vertical head plane approximately equal to the angle the original image now made with it. This point is called the "two-image" point, and the angle that the image makes with the vertical head plane at this point is called the "cross-over" angle. It is near the maximum displacement that phase will produce with the particular wave-length under observation.

After this "two-image" point has been noted, the head is still turned towards the left until the new image appears directly in front. This point can usually be found within

1° or 2°. The procedure is repeated to the right.

The results obtained are as follows:—

#### With Note of Wave-length 51 inches.

Zero at 4° left.

"Two-image" point at 57° left, no such point to the right.

"Cross-over angle" from 90° right (wide image) to 90° left (wide image). These images were over several degrees

of arc to right and left of 90°.

The "two-image" point  $57^{\circ}$  left, if we take it as occurring at a difference of phase equal to half a wave-length, and reckon from the zero at  $4^{\circ}$  left, gives us  $2(31 \sin 53^{\circ}) = 49.6$  inches as the wave-length.

With Note of Wave-length 40 inches.

Zero at 2° left.

"Two-image point" at 40° left and 38° right.

"Cross-over angle" from 90° right (wide image) to 90° left (wide image).

Taking 39° for the mean position of the two-image point,

we get  $2(31 \sin 39^{\circ}) = 39$  inches as the wave-length.

#### Note of Wave-length 27.6 inches. Zero at 4° left.

"Two-image point"... 22° r. and 30° l. (mean 26°). New images ......... 51° r. and 55° l. (mean 53°).

Cross-over angle from 50° right to 40° left and from 40° left to 40° right.

Wave-length from "two-image point"

 $=2 \times 31 \sin 26^{\circ} = 27.3$  inches.

Wave-length from new images

 $=31 \sin 53^{\circ} = 24.8$  inches.

## Note of Wave-length 19.4 inches.

Zero at 0°.

"Two-image point... 19° l. and 16° r. (mean  $17\frac{1}{2}$ °). New images ....... 42° l. and 46° r. (mean 44°).

Cross-over angle ... 36° r. to 36° l.

and  $36^{\circ}$  l. to  $36^{\circ}$  r.

Wave-length from "two-image point"  $= 2 \times 31 \sin 17\frac{1}{2}$ ° = 18.6 inches.

Wave-length from new images

 $=31 \sin 44^{\circ} = 21.4$  inches.

## Note of Wave-length 13.8 inches.

Zero at 0°.

"Two-image point"... 17° l., 17° r.

New images ............ 29° l., 62° l., 29° r., 68° r.

Cross-over angle ..... 18° to 18°.

Wave-length from "two-image point"

 $=2 \times 31 \sin 17^{\circ} = 18$  inches.

Wave-length from new images

 $=31 \sin 29^{\circ} = 14.9 \text{ inches.}$ 

and  $\frac{31 \sin 65^{\circ}}{2} = 14.1$  inches.

## Note of Wave-length 10.4 inches.

Zero at 3° r.

"Two-image point"... 13° l., 18° r., 41° l.

New images ........... 24° l., 23° r., 50° l.

Cross-over angle .....  $15^{\circ}$  to  $15^{\circ}$ .

Wave-length from first pair of two-image points  $=2(31 \sin 15\frac{1}{2}^{\circ})=16.7$  inches.

From first pair of new images

 $=31 \sin 23\frac{1}{2}$ ° = 12.4 inches.

From next image

$$=\frac{31 \sin 53^{\circ}}{2} = 12.4$$
 inches.

Below this wave-length the images were too near together to have their position clearly determined, the sound of one image confusing the apparent position of the other image.

Sometimes it appeared as if three images were in the field together, then the one nearest the source would appear the loudest and draw off the attention from, and apparently obscure the image directly in front of the observer.

The tubes were shortened so that the distance between the

centres of their ends was reduced to 15 inches.

With this pair of shortened tubes the following results were obtained:—

Wave-length 10.4 inches.

Zero at  $0^{\circ}$ .

"Two-image point"...  $22^{\circ}$  l.

New images at ....... 41° l. & 40° r.

Cross-over angle ..... 20° l. to 20° r.

Here the two images were heard with the head facing anywhere over the arc from 12° r. to 30° r. and from 12° l.to 30° l.

Wave-length by two-image point

 $=2 \times 15 \sin 22^{\circ} = 11.1$  inches.

Wave-length by new images

 $=15 \sin 40\frac{1}{2}$  = 9.8 inches.

Wave-length 8 inches.

"Two-image point"—two images were evident during nearly the whole range—there were practically always two and sometimes three images evident, though I had some doubts whether the central image was always real or a result of attention to the two side images.

New images..... 24° 1. & 21° r.

Cross-over angle 12°, i. e. the maximum angle of displacement was 12°.

Wave-length by new images =  $15 \sin 22\frac{1}{2}$  = 5.7 inches.

So far the tubes had been used with the full aperture—a circle of 2 inches diameter. Now they were closed by disks luted on with modelling-clay—the disks being perforated by holes  $\frac{6}{10}$  of an inch in diameter.

#### Note of Wave-length 6:4 inches.

Zero 4° l.

Images at 24° l. and 22° r.; but now three images could always apparently be heard together when facing one of them. When blowing the note hard the central image could be heard most strongly, but as the sound gradually ceased the central image died away, first leaving the impression that the two side images only existed.

Cross-over angle-or maximum angle of displacement of

image about 9°.

Wave-length by new images =  $15 \sin 23^{\circ} = 5.8$  inches.

#### Note of Wave-length 5.8 inches.

Zero at 0°.

Images at 16° l, and 14° r.

When facing the image at 16° l. the image further to the left seemed stronger and tended to draw off one's attention. When facing 14° r. the image at the source, which now appears only about 8° to the left, tends to obscure the image in front at 14° r.

Maximum displacement 6° or 8°.

Wave-length by images = 15 sin 15° = 3.9 inches.

#### Note of Wave-length 4.4 inches.

Here it was very difficult to determine even approximately the position of an image, the one to the left of the two or three in the field of view seeming the loudest as a rule. I thought I had images in front, however, at 8° r., 10° l., 22° l., 36° l., but it was impossible to distinguish between having an image directly in front and having a two-image point in front. I only felt sure that phase was still playing a part in fixing the maxima and minima which gave rise to the centres of the sound images.

From the measurements of the maximum angle of displacement that I had taken in the above experiments it would seem that for wave-lengths below 20 inches the angle of

displacement \* was very roughly proportional to the wavelength—for a wave-length of 4.4 inches the displacement

would only be  $5^{\circ}$  or  $6^{\circ}$ .

Now, to produce a difference of phase of half a wave-length the head, without the tubes, would have to be turned through about 23°—so if the head faced the source and was then turned to one side or the other, the image would appear to following the turning of the head if the intensity remained the same at the two ears, and when the head had turned through 23° the image of the source would have turned through 17°—this 17° must be compensated for by change of intensity at the two ears. As a matter of fact I am inclined to think that in the case of the higher notes—perhaps in the case of all notes—the zone or are in which the soundinage appears is settled by the relative intensity at the two ears; the actual position of the images within this zone being produced by the maxima and minima within it produced by phase-difference at the ears.

In order to explain the existence of a movable image of the sound within this zone, we may suppose that the transmission of the sound impulse through some specialized part of the auditory apparatus or brain takes a definite time from each ear, and that the point where the impulses meet is the focus

that gives rise to the sensation of a sound-image.

To explain the existence of two images, and perhaps three, we may suppose  $\alpha$  and  $\beta$  to be the crests of two successive waves; then, if the observer is facing the source, the crests of  $\alpha$  arriving at the ear simultaneously produce an image at the centre of the sound-zone;  $\alpha$  at the right ear and  $\beta$  at the left give an image to the right of the centre, and  $\alpha$  at the left ear and  $\beta$  at the right give an image to the left of the centre.

If two equal tubes be applied to the ears, one with aperture 2 inches in diameter, and the other of  $_{10}^{6}$  of an inch, and both apertures be turned square on to the source, I find a deflexion of  $20^{\circ}$  to be produced in the sound-zone, and within

this the image moves about as before.

In order to determine whether intensity affected the position of the image when notes of medium pitch were concerned, one ear-tube was closed by a disk of aluminium luted on with clay. A hole was made through the centre of this disk, through which hole a cylinder of paper, 2 inches

<sup>\*</sup> Further experiments with wave-lengths down to 2 inches would, however, seem to indicate that this law does not hold even roughly for short wave-lengths, the displacement being much larger than this law would give.

long and  $\frac{1}{2}$  inch in diameter, was inserted; the area of this tube was about  $\frac{1}{25}$  of the area of the ear-tube and it projected  $\frac{1}{4}$  inch beyond the disk. The outer  $2\frac{1}{2}$  inches of the tube was very loosely plugged with cotton-wool to suppress resonance.

A series of experiments was made. In one set the ear tube without the perforated disk was used, in the other the tube was used with the disk attached.

The tube was placed over the one ear, the other ear being free; the head faced the source of sound, and the apparent angular displacement of the image was noted.

The results are given in the following Table:—

Note of Wave-length 27.6 inches.

	Tube applied t	o the Right ear.	Tube applied to the Left ear.		
Length of tube applied to the ear.	Angular displacement without perforated disk.		Angular dis- placement without per- forated disk.	Angular dis- placement with per- forated disk.	
Inches.					
4	12° l.	30° 1.	2° r.	10° r.	
6		36° l.	16° r.	14° r.	
9		60° l. & 45° r.	22° r.	30° r.	
12	60° 1. & 50° r.	24° r.	32° r.	12° l.	
15	0.30	20° r.	34° r.	36° 1,	
18	28° r.	14° r.	45° r. & 50° l.	30° 1.	
21	10° r.	00	40° l.	0°	
$22\frac{1}{2}$	00	10° 1.		2° r.	
26	16° l.	40° 1.	0° 1.	18° r.	

From this it is evident that intensity plays an important part in fixing the position of the sound-image when there is a great difference of intensity at the two ears.

Another experiment which shows the part played by intensity, and yet how largely the apparent position is affected by phase at the same time, was tried. In this case the observer's left ear was towards the source of sound, the vertical plane through the ears passing through the source. Ear-tubes of various lengths were applied to the right ear, and the head was kept fixed, the angle of displacement being noted.

The results are as follow:--

The source is considered zero—the point in front of the

observer is  $+90^{\circ}$ , the point directly behind is  $-90^{\circ}$  (where not marked negative the angle is to be taken as positive).

					-				
Length of ear-tube.	Angular dis- placement.	Lengtl ear-ti		Angular d placemen			gth of -tube.	Angular o	
Inches. 3 5 6 7 8 9	-60° +60 55 45 36 0	4 5 6 7 8 9	s.	0° 45 80 75 60 50 45	And the second s	Incl 4 6 8 9 10 12 14	nes.	0° 8 8 90 90 80 70	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	80 70 60 36 0 10	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		36 16 0 20 40 60	de la company de	$   \begin{array}{c}     15 \\     16 \\     17 \\     18 \\     19\frac{1}{2} \\     20\frac{1}{2}   \end{array} $		60 60 50 30 12 0	e
16 10  And it now always remains within 20° of 0.		18 19 21		45 38 20 0 50				ne an gle of ent is smal	

I simply record these results without attempting any explanation, beyond suggesting that sound-conduction through the bone and some portion of the brain-substance may perhaps play a part in fixing the sound-zone when the image is perceived.

It is to be remarked that as no special care was taken to suppress resonance in the above experiments, it is probable

that some of the results are affected by it.

In order to determine the amount of displacement produced by a difference of phase in the arrival of sound at the ears, a pair of tubes 6 inches long and  $2\frac{2}{10}$  inches in diameter were taken. A pair of flat rectangular plates 4½ inches by 2½ inches were also taken, and in each of them a slit  $1\frac{1}{2}$  inches long and  $\frac{6}{10}$  inch wide was cut across symmetrically near the centre. These plates were luted on to the outer ends of the ear-tubes with modelling-clay, and were so arranged that the central line of the slit was 6 of an inch distant from the axis of the tube.

The observer faced the source of sound and applied these tubes to the ears, the slit of one tube being vertical and nearer the source, the other vertical and further from the source.

The position of the image was noted, and the tubes were then rotated through 180° about their axis, and the position of the image again noted.

This arrangement made the conditions at both ears precisely the same as regards resonance and intensity for both observations, the only difference being that there was a difference of 2.4 inches in the length of the path of sound to the two ears in the two cases.

With this apparatus the results with two observers, myself and Mr. O. B. Clarke, were as follows:—

Wave-length	Angular displacement of image.				
of sound.	Observer O. B. C.	Observer T. J. B.			
Inches.	18°	120			
26.8	18	14			
19.4	20	14			
13.8	18	14			
10.4	24	16			
8.0	18	14			
6.4	18	12			

It is remarkable that the angle of displacement should remain nearly the same with such a wide variation in wavelength.

Now if we take the diameter of the head through the ears to be  $5\frac{1}{2}$  inches, a movement of the head of  $25^{\circ}$  would make a difference of  $2\frac{4}{10}$  inches in the distances of the ears from the source of sound.

Assuming that when the head is turned through 25° the direction of the source is indicated exactly by the sensation of the image, this experiment shows that in the case of one observer an average of 6°, and in the case of the other observer of 11°, had to be made up by the displacement of the sound-image due to intensity or other cause. As regards myself, I find that when my right ear is turned partly towards the source of sound and with eyes shut I point to it, I underestimate the angle from the symmetrical head-plane for sounds of 24 inches wave-length and over, and overestimate the angle when the left ear is turned towards the source.

With regard to the general intensity of the sound, I find that when the sound is fairly loud the apparent

direction, when using ear-tubes and facing the source, remains almost the same when the sound becomes louder, the angle of displacement becoming, if anything, somewhat smaller. In the case of the notes of greater frequency, however, the sound when dying away will, in my case, move through a considerable angle to the left, if its original position is near the source to start with—this is probably due to my left ear being more sensitive for feeble shrill sounds than the right ear.

In connexion with these methods of examining soundimages, an interesting experiment is to take two tubes of 2 inches or more in diameter, one say 12 inches long and the other 4 inches, and listen to a band of three or four instruments played in the open—the notes will be found to be scattered over a wide range, most being to the side of the short tube, some being in front and some being to the side

of the long tube.

In listening with such a pair of tubes to two dogs furiously barking, the effect is at first quite alarming—one seems to be in the middle of a pack of dogs some of which are rushing viciously at one's throat, Preferably the tubes should be of metal sheet, and it is best, though not necessary, to surround them with a sheet of some rubber cloth or composition.

It remains to say something about the interference of trains of waves after reflexion in producing a change in the

position of the image.

In one experiment, an organ-pipe was placed 5 feet from a flat wall and the observer stationed on a line, making an angle of 30° with the wall, through the foot of the perpendicular from the organ-pipe on the wall. There was more difficulty in settling the direction than when there was no wall, and the apparent position seemed to be at the foot of the perpendicular on the wall: with other positions of the observer, the apparent image of the source varied between the source and this point.

When the positions of the observer and the source were interchanged, I obtained these results when working with a

note of wave-length 26.8 inches.

Source of sound 40 feet distant.

Ear 30 inches from the wall—the only image lay on a line from the ear parallel to the wall.

(The image of the first harmonic of the stopped pipe was displaced 10°.)

As the head was moved nearer to the wall, the image

moved gradually nearer to the source and arrived at the source when the ear was 16 inches from the wall.

A similar experiment with a note of wave-length 19.4 inches gave the image:—

on line parallel to the wall, with ear distant 17, 39, 61 inches at the source, with ear distant 24, 48, 58 inches 40° from the wall, with ear distant 32, 52 inches.

From these experiments it is clear that in noting the direction of a fog-horn at sea the observer should be well away from any reflecting surfaces of any kind. (In one experiment an umbrella held to one side of the head at a distance of 2 feet displaced the sound-image 20°.) I find that it adds to correctness in fixing the direction to have a flat board slung on the shoulders vertical and parallel to the axis of the ears. This increases the intensity in front and shuts off sound from the rear. I think it would also be better to have two short blasts of 3 seconds each, every half minute, at sea, rather than a long blast every minute.

Also fog-horns should be placed well above any reflecting surfaces, but it might add to their carrying power if a large disk or sounding-board was placed horizontally directly over

them,

XXXII. On certain Bessel Integrals and the Coefficients of Mutual Induction of Coaxial Coils. By T. H. HAVELOCK, M.A., D.Sc.; Fellow of St. John's College, Cambridge; Lecturer in Applied Mathematics, Armstrong College, Newcastle-on-Tyne\*.

THE calculation of coefficients of mutual induction has been discussed by several writers from the time of Maxwell to the present, more accurate expressions being required as experimental methods have become more refined. The expressions are generally in one of two forms: they are either given in elliptic integrals, in which case numerical calculations are tedious, or given by a certain number of terms of a series.

The present paper brings forward another method of expressing the coefficients, namely in terms of integrals involving Bessel functions; series are obtained from these integrals, their general terms found, and their convergence tested. In certain cases series are obtained which seem to be simpler and better adapted for numerical calculation than

<sup>\*</sup> Communicated by the Author.

those in use at present; the cases examined are those involving two coaxial coils treated simply as cylindrical current-sheets. The Bessel integrals used here occur frequently in other physical problems; it has been thought better to give the investigation of these separately in the first section, where the series are obtained and examined independently of the applications made later.

#### § 1. Some Integrals involving Bessel Functions.

The integrals which we have to evaluate are of the type

$$\mathbf{I} = \int_{0}^{\infty} e^{-p\mu} \mathbf{J}_{1}(\mu) \mathbf{J}_{1}(\lambda \mu) \mu^{-n} d\mu,$$

and we require their expression in series suitable for large and for small values of p.

When p is zero we have the following known integrals:—

$$\int_{0}^{\infty} J_{1}^{2}(\mu) \frac{d\mu}{\mu^{2}} = \frac{4}{3\pi}; \quad (2)$$

$$\int_{0}^{\infty} J_{1}(\mu a) J_{1}(\mu b) \frac{d\mu}{\mu} = \frac{1}{2} \frac{a}{b}, \quad b > a . \qquad (3)$$

$$\begin{split} \int_{0}^{\infty} \mathbf{J}_{1}(\mu a) \mathbf{J}_{1}(\mu b) \frac{d\mu}{\mu^{2}} &= \frac{2}{\pi a b} \int_{0}^{a} \sqrt{(a^{2} - c^{2})(b^{2} - c^{2})} dc, \quad b > c \\ &= \frac{2}{3\pi a} \left\{ (b^{2} + a^{2}) \mathbf{E} - (b^{2} - a^{2}) \mathbf{F} \right\}, \end{split}$$

where E, F are complete elliptic functions of modulus a/b. Also, putting k for a/b, we have in the last case

$$\int_{0}^{\infty} J_{1}(\mu a) J_{1}(\mu b) \frac{d\mu}{\mu^{2}} = a \left( \frac{1}{2} - \frac{1}{16} k^{2} - \frac{1}{128} k^{4} - \frac{5}{2048} k^{6} - \dots \right)$$

$$= -a \sum_{r=0}^{\infty} \frac{\{1 \cdot 3 \cdot 5 \cdot \dots (2r-3)\}^{2} (2r-1)}{2^{2r+1} r! (r+1)!} k^{2r}. \quad (4)$$

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This series is convergent for k less than unity; it converges rapidly, and in most cases we shall find the first three terms sufficient.

Consider now the integral

$$I = \int_{0}^{\infty} e^{-p\mu} J_{1}^{2}(\mu) d\mu. \qquad (5)$$

If p is large we can easily find a suitable series for I in ascending inverse powers of p; we substitute for the Bessel function its equivalent series in ascending powers of  $\mu$  and then integrate each term separately. Then, since we have

$$\mathbf{J}_{1^{2}}(\mu) = \sum_{s=0}^{\infty} (-1)^{s} \frac{(2s+2)!}{s!(s+2)!\{(s+1)!\}^{2}} \left(\frac{\mu}{2}\right)^{2s+2},$$

and

$$\int_{0}^{\infty} e^{-p\mu} \mu^{2s} d\mu = \frac{(2s)!}{p^{2s+1}},$$

we obtain the series

$$\int_{0}^{\infty} e^{-p\mu} J_{1}^{2}(\mu) d\mu = \sum_{s=0}^{\infty} (-1)^{s} \frac{\{(2s+2)!\}^{2}}{2^{2s+2} s! (s+2)! \{(s+1)!\}^{2}} \frac{1}{p^{2s+3}} ; \quad (6)$$

$$\int_{0}^{\infty} e^{-p\mu} J_{1}^{2}(\mu) \frac{d\mu}{\mu} = \sum_{s=0}^{\infty} (-1)^{s} \frac{(2s+1)!(2\bar{s}+2)!}{2^{2s+2} s!(s+2)! \{(s+1)!\}^{2}} \frac{1}{p^{2s+2}}; \quad (7)$$

$$\int_{0}^{\infty} e^{-p\mu} J_{1}^{2}(\mu) \frac{d\mu}{\mu^{2}} = \sum_{s=0}^{\infty} (-1)^{s} \frac{(2s)!(2s+2)!}{2^{2s+2}s!(s+2)!\{(s+1)!\}^{2}} \frac{1}{p^{2s+1}}$$

$$= \frac{1}{4} \frac{1}{p} - \frac{1}{8} \frac{1}{p^{3}} + \frac{5}{32} \frac{1}{p^{5}} - \frac{35}{128} \frac{1}{p^{7}} + \dots$$
 (8)

The series are convergent for p > 2. Further we have \*

$$J_{1}(\mu)J_{1}(\lambda\mu) = \lambda \sum_{s=0}^{\infty} (-1)^{s} \frac{F(-s-1, -s, 2, \lambda^{2})}{s!(s+1)!} \left(\frac{\mu}{2}\right)^{2s+2}, \quad (9)$$

<sup>\*</sup> Nielsen, Cylinderfunctionen, p. 20.

where  $\lambda < 1$ , and F is the hypergeometric series given by

$$\mathbf{F}(a, b, c, x) = 1 + \frac{ab}{c}x + \frac{a(a+1)b(b+1)}{2! c(c+1)}x^{2} + \frac{a(a+1)(a+2)b(b+1)(b+2)}{3! c(c+1)(c+2)}x^{3} + \dots$$

Then, using the same method, we obtain series for more general integrals suitable for large values of p. We obtain thus

$$\int_{0}^{\infty} e^{-p\mu} J_{1}(\mu) J_{1}(\lambda \mu) d\mu = \lambda \sum_{s=0}^{\infty} (-1)^{s} \frac{(2s+2)! F(-s-1, -s, 2, \lambda^{2})}{s! (s+1)! 2^{2s+2}} \frac{1}{p^{2s+3}}; \quad (10)$$

$$\int_{0}^{\infty} e^{-p\mu} J_{1}(\mu) J_{1}(\lambda \mu) \frac{d\mu}{\mu} = \lambda \sum_{s=0}^{\infty} (-1)^{s} \frac{(2s+1)! F(-s-1, -s, 2, \lambda^{2})}{s! (s+1)! 2^{2s+2}} \frac{1}{p^{2s+2}}; \quad (11)$$

$$\int_{0}^{\infty} e^{-p\mu} J_{1}(\mu) J_{1}(\lambda \mu) \frac{d\mu}{\mu^{2}} = \lambda \sum_{s=0}^{\infty} (-1)^{s} \frac{(2s)! F(-s-1, -s, 2, \lambda^{2})}{s! (s+1)! 2^{2s+2}} \frac{1}{p^{2s+1}}$$

$$= \lambda \left[ \frac{1}{4} \frac{1}{p} - \frac{1}{16} (1+\lambda^{2}) \frac{1}{p^{3}} + \frac{1}{32} (1+3\lambda^{2}+\lambda^{4}) \frac{1}{p^{5}} - \frac{5}{256} (1+6\lambda^{2}+6\lambda^{4}+\lambda^{6}) \frac{1}{p^{7}} + \dots \right]. \quad (12)$$

To obtain series suitable for small values of p we have

$$y = \int_0^{\infty} e^{-p\mu} J_1^2(\mu) d\mu$$

$$= -\frac{1}{\pi} \int_0^{\pi} \cos \alpha d\alpha \int_0^{\infty} e^{-p\mu} J_0(2\mu \cos \frac{1}{2}\alpha) d\mu$$

$$= -\frac{2}{\pi} \int_0^{\frac{\pi}{2}} \frac{\cos 2\theta d\theta}{\sqrt{p^2 + 4 \cos^2 \theta}}.$$

The summation in this integral is now divided into two parts, one between the limits 0 and  $\frac{\pi}{2} - \epsilon$  and the other between  $\frac{\pi}{2} - \epsilon$  and  $\epsilon$ ;  $\epsilon$  may be taken indefinitely small

ultimately, but at present it is regarded as indefinitely larger than p.

Then we have

In  $y_1$  we write, as far as terms in  $p^4$ ,

$$\frac{2\cos 2\theta}{\sqrt{p^2+4\cos^2\theta}} = \frac{\cos 2\theta}{\cos \theta} \left[ 1 - \frac{1}{8} \frac{p^2}{\cos^2\theta} + \frac{3}{128} \frac{p^4}{\cos^4\theta} \right].$$

Then we integrate the terms separately, substitute the imits 0 and  $\frac{\pi}{2} - \epsilon$ , and assuming  $\epsilon$  small we expand as far as necessary; we obtain thus

$$y_{1}=2+\log\frac{1}{2}\epsilon-\frac{1}{8}p^{2}\left(\frac{1}{12}-\frac{1}{2\epsilon^{2}}-\frac{3}{2}\log\frac{1}{2}\epsilon\right)$$

$$+\frac{3}{128}p^{4}\left(-\frac{133}{1440}+\frac{7}{12\epsilon^{2}}-\frac{1}{4\epsilon^{4}}-\frac{5}{8}\log\frac{1}{2}\epsilon\right). \quad (14)$$

In the second integral  $y_2$ , p is small compared with  $\theta$  throughout the range; we substitute for  $\cos 2\theta$  and  $\sin \theta$  their expansions in powers of  $\theta$  and expand by the binomial theorem. We obtain

$$y_2 = \int_0^\epsilon \left[ 1 - 2\theta^2 + \frac{2}{3} \theta^4 + \frac{2}{3} \frac{\theta^4}{p^2 + 4\theta^2} - \frac{64}{15} \frac{\theta^6}{p^2 + 4\theta^2} + \frac{2}{3} \frac{\theta^8}{(p^2 + 4\theta^2)^2} \right] \frac{d\theta}{\sqrt{p^2 + 4\theta^2}},$$

including all parts which will give terms containing  $p^4$  on integration. Integrating the parts separately and expanding as far as  $p^4/\epsilon^4$  we find

$$= \frac{1}{2} \left( 1 + \frac{3}{16} p^2 - \frac{15}{1024} p^4 \right) \left( \log \frac{4\epsilon}{p} + \frac{p^2}{16\epsilon^2} - \frac{3p^4}{512\epsilon^4} \right) - \frac{\epsilon^4}{144} \left( 1 - \frac{3p^2}{8\epsilon^2} + \frac{15p^4}{128\epsilon^4} \right)$$

$$- \left( \frac{3}{8} \epsilon^2 + \frac{5}{64} \epsilon^4 - \frac{15}{512} p^2 \epsilon^2 \right) \left( 1 + \frac{p^2}{8\epsilon^2} - \frac{p^4}{128\epsilon^4} \right)$$

$$- \left( \frac{1}{12} \epsilon^2 - \frac{31}{240} \epsilon^4 \right) \left( 1 - \frac{p^2}{8\epsilon^2} + \frac{3p^4}{128\epsilon^4} \right). \qquad (15)$$

Substituting these values of  $y_1$  and  $y_2$  in (13) we find that the terms in  $\log \epsilon$  and inverse powers of  $\epsilon$  cancel; then making  $\epsilon$  indefinitely small the terms involving positive powers of  $\epsilon$  vanish and we obtain as far as terms in  $p^4$ 

$$y = \int_0^\infty e^{-p\mu} J_1^2(\mu) d\mu$$

$$= \frac{1}{\pi} \left\{ \left( 1 + \frac{3}{16} p^2 - \frac{15}{1024} p^4 \right) \log_e \frac{8}{p} - 2 - \frac{1}{16} p^2 + \frac{31}{2048} p^4 \right\}. (16)$$

Further, if we integrate (11) with respect to p and put the constant of integration equal to  $\frac{1}{2}$  on account of (1), we obtain

$$\begin{split} \int_{0}^{\infty} e^{-p\mu} \mathbf{J}_{1}^{2}(\mu) \frac{d\mu}{\mu} \\ &= -\frac{1}{\pi} \left\{ \left( p + \frac{1}{16} p^{3} - \frac{3}{1024} p^{5} \right) \log_{\theta} \frac{8}{p} - \frac{\pi}{2} - p + \frac{5}{2048} p^{5} \right\}. (17) \end{split}$$

Integrating again with respect to p and taking account of (2) we find

$$\begin{split} \int_{0}^{\infty} e^{-p\mu} \mathbf{J}_{1}^{2}(\mu) \frac{d\mu}{\mu^{2}} &= \frac{1}{\pi} \left\{ \frac{1}{2} p^{2} \left( 1 + \frac{1}{32} p^{2} - \frac{1}{1024} p^{4} \right) \log_{e} \frac{8}{p} \right. \\ &\quad + \frac{4}{3} - \frac{\pi}{2} p - \frac{1}{4} p^{2} + \frac{1}{256} p^{4} + \frac{1}{3072} p^{6} \right\} \\ &= \frac{1}{\pi} \left\{ \frac{4}{3} - \frac{\pi}{2} p + \frac{1}{2} p^{2} \left( \log \frac{8}{p} - \frac{1}{2} \right) \right. \\ &\quad + \frac{1}{64} p^{4} \left( \log \frac{8}{p} + \frac{1}{4} \right) - \frac{1}{2048} p^{6} \left( \log \frac{8}{p} - \frac{2}{3} \right) \right\}. (18) \end{split}$$

In the same way, if  $p^2 + (1-\lambda)^2$  is small compared with  $\lambda$ , and if  $\lambda > 1$ , we obtain from (11) the more general expansion

$$\pi \lambda^{\frac{1}{2}} \int_{0}^{\infty} e^{-p\mu} J_{1}(\mu) J_{1}(\lambda \mu) d\mu$$

$$= \left[ 1 + \frac{3}{16} \frac{p^{2} + (1-\lambda)^{2}}{\lambda} - \frac{15}{1024} \left\{ \frac{p^{2} + (1-\lambda)^{2}}{\lambda} \right\}^{2} \right] \log 8 \sqrt{\frac{\lambda}{p^{2} + (1-\lambda)^{2}}}$$

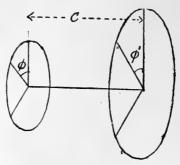
$$-2 - \frac{1}{16} \frac{p^{2} + (1-\lambda)^{2}}{\lambda} + \frac{31}{2048} \left\{ \frac{p^{2} + (1-\lambda)^{2}}{\lambda} \right\}^{2} . . (19)$$

Finally, integrating (19) with respect to p and taking account of (3) we can obtain a similar series for the integral

$$\int_0^\infty e^{-p\mu} J_1(\mu) J_1(\lambda \mu) \frac{d\mu}{\mu}. \qquad (20)$$

#### § 2. Mutual Induction of Single-layer Coil and Coaxial Circle.

If we have two coaxial circles of radii a and b, with a distance c between their planes, we have their coefficient of



mutual induction given by

$$\mathbf{M} = \iint \frac{\cos \epsilon}{r} ds \, ds' = \int_0^{2\pi} \int_0^{2\pi} \frac{ab \cos (\phi - \phi') \, d\phi \, d\phi'}{\sqrt{c^2 + a^2 + b^2 - 2ab \cos (\phi - \phi')}}$$

$$= \int_0^{2\pi} \int_0^{2\pi} ab \cos (\phi - \phi') \, d\phi \, d\phi' \int_0^{\infty} e^{-\lambda c} \mathbf{J}_0(\lambda \sqrt{a^2 + b^2 - 2ab \cos (\phi - \phi')}) \, d\lambda$$

$$= 4\pi^2 ab \int_0^{\infty} e^{-\lambda c} \mathbf{J}_1(\lambda a) \, \mathbf{J}_1(\lambda b) \, d\lambda. \qquad (21)$$

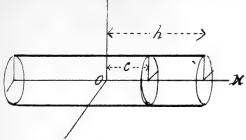
From the integrals (10) and (19) in the previous section series for M could be obtained suitable for c large or small compared with a or b. Further, if we have a single-layer solenoid of length 2h, radius b, and n turns of wire per unit length together with a concentric coaxial circle of radius a, less than b, we obtain their coefficient of mutual induction by integrating (21) with respect to c between the limits -h and +h. Hence we obtain

$$\mathbf{M} = 8\pi^2 abn \int_0^\infty (1 - e^{-\lambda h}) \, \mathbf{J}_1(\lambda a) \, \mathbf{J}_1(\lambda b) \, \frac{d\lambda}{\lambda}. \quad . \quad (22)$$

Using then the integrals given in (11) and (20) we have series suitable both for long and for short coils. However, in the latter case the difference between the radii of the coil and the circle must be small compared with one of them, and unless this holds series already in use probably give a better approximation than those obtained from (22)\*. Finally, if

<sup>\*</sup> Cf. E. B. Rosa, Bulletin of the Bureau of Standards, vol. iii. p. 209, 1907.

we have a solenoid of length 2h and radius a, and a circle of the same radius at a distance c from the central section of



the coil, we obtain from (16)

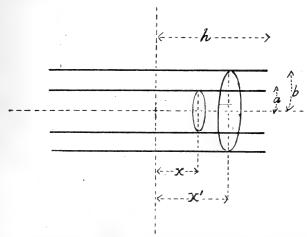
$$\mathbf{M} = 4\pi^{2}a^{2}n \int_{0}^{\infty} d\lambda \mathbf{J}_{1}^{2}(\lambda a) \left[ \int_{-h}^{c} e^{-\lambda(c-x)} dx + \int_{c}^{h} e^{-\lambda(x-c)} dx \right]$$

$$= 4\pi^{2}a^{2}n \int_{0}^{\infty} \left\{ 2 - e^{-\lambda(h+c)} - e^{-\lambda(h-c)} \right\} \mathbf{J}_{1}^{2}(\lambda a) \frac{d\lambda}{\lambda} . \qquad (23)$$

$$= 4\pi^{2}a^{2}n \left[ 1 - \int_{0}^{\infty} \left\{ e^{-\frac{h+c}{a}\mu} - e^{-\frac{h-c}{a}\mu} \right\} \mathbf{J}_{1}^{2}(\mu) \frac{d\mu}{\mu} \right]. \qquad (24)$$

Substituting for these integrals from (7) and (17) according as h+c and h-c are large or small compared with a, we can obtain series giving the induction through any section of a solenoid, whether it is a long or a short coil.

#### § 3. Two Coaxial Solenoids of Equal Length.



Suppose we have two single-layer coils of equal length 2h and of radii a and b, placed as in the figure; let  $n_1$  and

 $n_2$  be the number of turns of wire per unit length on the two cylinders. Then if we write |x-x'| for the absolute value of x-x', we have from (21)

$$\begin{split} \mathbf{M} &= 4\pi^2 a b n_1 n_2 \int_0^\infty \mathbf{J}_1(\mathbf{\lambda} a) \mathbf{J}_1(\mathbf{\lambda} b) d\mathbf{\lambda} \int_{-\hbar}^\hbar dx \int_{-\hbar}^\hbar dx' e^{-\mathbf{\lambda} \|\mathbf{x} - \mathbf{x}'\|} \\ &= 16\pi^2 a b n_1 n_2 \int_0^\infty \left\{ \frac{h}{\mathbf{\lambda}} - \frac{1}{2\mathbf{\lambda}^2} + \frac{1}{2\mathbf{\lambda}^2} e^{-2\hbar\mathbf{\lambda}} \right\} \mathbf{J}_1(\mathbf{\lambda} a) \mathbf{J}_1(\mathbf{\lambda} b) d\mathbf{\lambda}. \end{split}$$

With b>a and h>b, we use the series (3), (4) and (12); thus we find for the coefficient of mutual induction of the two coils:

$$\mathbf{M} = 8\pi^{2}abn_{1}n_{2} \left[ \frac{h}{b} - \frac{1}{2} + \frac{1}{16} \left( \frac{a}{b} \right)^{2} + \frac{1}{128} \left( \frac{a}{b} \right)^{4} + \frac{5}{2048} \left( \frac{a}{b} \right)^{6} + \dots \right]$$

$$+ \frac{1}{8} \frac{b}{h} - \frac{1}{128} \left( 1 + \frac{a^{2}}{b^{2}} \right) \left( \frac{b}{h} \right)^{3} + \frac{1}{1024} \left( 1 + 3\frac{a^{2}}{b^{2}} + \frac{a^{4}}{b^{4}} \right) \left( \frac{b}{h} \right)^{5}$$

$$- \frac{5}{2^{15}} \left( 1 + 6\frac{a^{2}}{b^{2}} + 6\frac{a^{4}}{b^{4}} + \frac{a^{6}}{b^{6}} \right) \left( \frac{b}{h} \right)^{7} + \dots \right] (25)$$

This gives an expression for M which is easy of calculation and rapidly convergent; moreover, from (4) and (12), additional terms in the two series within the brackets in (25) can be calculated if required from the general terms

$$\frac{\{1.3.5...(2r-3)\}^{2}(2r-1)}{2^{2r+1}r!(r+1)!}\left(\frac{a}{b}\right)^{2r}$$

and

$$(-1)^{s} \frac{(2s)! \operatorname{F}\left(-s-1,-s,2,\frac{a^{2}}{\overline{b^{2}}}\right)}{2^{4s+3} \, s! \, (s+1)!} \left(\frac{b}{h}\right)^{2s+1}.$$

We consider as a numerical illustration a case which has been used in comparing other similar series, namely:—

$$a=5 \text{ cm.}; b=10 \text{ cm.}; h=100 \text{ cm.}; n_1=n_2=n.$$

Then we have

$$\frac{h}{b} = 10$$
;  $\frac{b}{h} = \frac{1}{10}$ ;  $\frac{a}{b} = \frac{1}{2}$ ,

and from (25)

$$\mathbf{M} = 2000\pi^{2}n^{2} \left(10 - \frac{1}{2} + \frac{1}{2^{6}} + \frac{1}{2^{11}} + \frac{5}{2^{17}} + \dots + \frac{1}{80} - \frac{5}{2^{9}} + \frac{1}{10^{3}} + \dots \right).$$

Using the terms shown, we find that this gives

$$M/\pi^2 n^2 = 19057.28.$$
 . . . (26)

Further, by calculating a few more terms, we easily see that the result in (26) is correct as far as the figures shown. Other series for this case are those of Maxwell\* and Heaviside †, while a complete expression in elliptic functions has been given by Cohen ‡. In the last case, although an exact theoretical expression is found, yet in practice the accuracy depends upon tables of elliptic functions and upon the result of long and complicated calculations. These three expressions have been compared numerically by Rosa and Cohen & for the case used above; they give the following results for  $M/\pi^2 n^2$ :—

Maxwell's series	19057.25
Heaviside's series	19067:08
Cohen's elliptic-function formula	

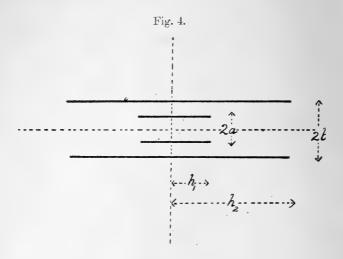
Comparing these with the result given in (26) we infer that the two latter formulæ do not give better results than Maxwell's, at least when the ratio of length to diameter is large; Cohen's formula is applicable to all values of this ratio, but it is not suitable for calculation. The series given in (25) appears somewhat simpler than Maxwell's; it is convergent for all coils with the length greater than the radius of the outer coil, and as one knows the general term of the series the result can be calculated to any required degree of accuracy; it can easily be verified that the series converges quite rapidly even for coils whose length is not much greater than their breadth.

<sup>\*</sup> Maxwell, 'Electricity and Magnetism,' vol. ii. § 678. † Heaviside, 'Electrical Papers,' vol. ii. p. 277. † Cohen, Bulletin of the Bureau of Standards, vol. iii. p. 295 (1907).

<sup>§</sup> Rosa and Cohen, Bulletin of the Bureau of Standards, vol. iii. p. 316 (1907).

#### § 4. Short Coil inside a Long Coil.

Another case is that of a coil of length  $2 h_1$  within concentric coaxial coil of length  $2 h_2$ , as in the figure.



Then if  $n_1$  and  $n_2$  are the turns per unit length, we have

$$\mathbf{M} = 4 \, \pi^2 \, ab \, n_1 \, n_2 \int_0^\infty \mathbf{J}_1(\lambda a) \mathbf{J}_1(\lambda b) \, d\lambda \int_{-h_1}^{h_1} dx \int_{-h_2}^{h_2} e^{-\lambda ||x-x'||} \, dx'$$

$$= 8 \, \pi^2 \, ab \, n_1 n_2 \left[ \frac{a}{b} h_1 - b \int_0^\infty \left( e^{-\mu \frac{h_2 - h_1}{b}} - e^{-\mu \frac{h_2 + h_1}{b}} \right) \mathbf{J}_1(\mu) \mathbf{J}_1\left(\frac{a}{b} \mu\right) \frac{d\mu}{\mu^2} \right], \quad (27)$$

Hence, if  $h_2 - h_1$  is large compared with b, a suitable series can be obtained by using (12) in these two integrals. We find

$$\begin{split} \mathbf{M}/8\pi^{2}abn_{1}n_{2} &= \frac{a}{b}h_{1} - a\left[\frac{1}{4}\left(\frac{b}{h_{2} - h_{1}} - \frac{b}{h_{2} + h_{1}}\right)\right. \\ &\left. - \frac{1}{16}\left(1 + \frac{a^{2}}{b^{2}}\right)\left\{\left(\frac{b}{h_{2} - h_{1}}\right)^{3} - \left(\frac{b}{h_{2} + h_{1}}\right)^{3}\right\} \\ &\left. + \frac{1}{32}\left(1 + 3\frac{a^{2}}{b^{2}} + \frac{a^{4}}{b^{4}}\right)\left\{\left(\frac{b}{h_{2} - h_{1}}\right)^{5} - \left(\frac{b}{h_{2} + h_{1}}\right)^{5}\right\} - \dots\right]. \end{split}$$

The general term can be obtained from (12) if required:

for purposes of calculation the series can be written in the following way:

$$\begin{split} \mathbf{M}/8\pi^{2}a^{2}n_{1}n_{2} &= h_{1} - b^{2} \left[ \frac{1}{4}(u - v) - \frac{1}{16}d(u^{3} - v^{3}) \right. \\ &+ \left. \frac{1}{32}(c^{2} + d^{2})(u^{5} - v^{5}) - \frac{5}{256}d(3c^{2} + d^{2})(u^{7} - v^{7}) + \ldots \right], \quad . \quad (28) \end{split}$$

where

$$c=ab$$
;  $d=a^2+b^2$ ;  $u=\frac{1}{h_2-h_1}$ ;  $v=\frac{1}{h_2+h_1}$ .

We shall test this formula by the following numerical example which has been used to compare other series:

$$h_2=15$$
 cm.;  $h_1=2.5$  cm.;  $b=5$  cm.;  $a=4$  cm.;  $n_1=10$ , and  $n_2=40$  turns per cm.

Then we substitute in (28) the following values:

$$c=20$$
;  $d=41$ ;  $u=\frac{2}{25}$ ;  $v=\frac{2}{35}$ .

Calculating the terms shown, we find to the order indicated

$$M = .0012000 \text{ henry.}$$

From the form of the series we see that this is larger than the true value; and in fact, by taking an extra term we find to the same order

$$M = .0011999 \text{ henry.}$$

Rosa and Cohen \* have calculated the same example by three different series using a similar number of terms and give the results:—

M. Series.

:001199896 ..... Roiti.
:00119990 ..... Searle and Airey.
:00119989 ..... Russell.

### § 5. Short Coil outside a Long Coil.

With the same notation, suppose  $h_2$  is small and  $h_1$  large. It has been thought that in this case the formula for M is

different from before and more complicated. But we have

$$\mathbf{M} = 4\pi^{2}abn_{1}n_{2}\int_{0}^{\infty}\mathbf{J}_{1}(\lambda a)\mathbf{J}_{1}(\lambda b)d\lambda \int_{-h_{1}}^{h_{1}}dx \int_{-h_{2}}^{h_{2}}e^{-\lambda |x-x'|}dx'$$

$$= 8\pi^{2}abn_{1}n_{2}\left[\frac{a}{b}h_{2} - b\int_{0}^{\infty}\left(e^{-\mu\frac{h_{1}-h_{2}}{b}} - e^{-\mu\frac{h_{1}+h_{2}}{b}}\right)\mathbf{J}_{1}(\mu)\mathbf{J}_{1}\left(\frac{a}{b}\mu\right)\frac{d\mu}{\mu^{2}}\right]. \tag{29}$$

Comparing this with (27) we see that  $h_1$  and  $h_2$  are merely interchanged; so that there is a similar series to (28) for this case also.

#### § 6. Self-induction of a Cylindrical Coil.

As a final example we consider the self-induction of a single-layer coil; then if we have

$$2h =$$
length of coil;  $a =$ radius;

N = 2nh = total number of turns of wire;

we can easily deduce from the integrals in § 4 an expression for the self-induction of a coil in the form

$$L = 4\pi^{2} a^{2} \frac{N^{2}}{h^{2}} \int_{0}^{\infty} \left\{ \frac{h}{\lambda} - \frac{e^{-\lambda h}}{\lambda^{2}} \sinh(\lambda h) \right\} J_{1}^{2}(\lambda a) d\lambda$$

$$= 2\pi^{2} \frac{a^{2} N^{2}}{h} \left[ 1 - \frac{4}{3\pi} \frac{a}{h} + \frac{a}{h} \int_{0}^{\infty} e^{-\frac{2h}{a} \mu} J_{1}^{2}(\mu) \frac{d\mu}{\mu^{2}} \right]. \quad (30)$$

For the integral in (30) we can now use one of the series (8) or (18).

If h > a, we have from (8) the series

$$I_{l} = 2\pi \frac{a^{2}N^{2}}{h} \left\{ 1 - \frac{4}{3\pi} \frac{a}{h} + \frac{1}{8} \left( \frac{a}{h} \right)^{2} - \frac{1}{2^{6}} \left( \frac{a}{h} \right)^{4} + \frac{5}{2^{1_{0}}} \left( \frac{a}{h} \right)^{6} - \frac{35}{2^{1_{0}}} \left( \frac{a}{h} \right)^{8} + \dots \right\}, \quad (31)$$

where the general term is given by

$$\frac{(2s!) (2s+2)!}{s! (s+2)! \{(s+1)!\}^2 2^{4s+3}} \left(\frac{a}{h}\right)^{2s+2}.$$

The first four terms of this series have been obtained by a different method by Russell\*. We see that the series in general is simple and rapidly convergent for coils whose length is greater than their width.

<sup>\*</sup> Russell, Philosophical Magazine, vol. xiii. p. 445 (1907).

For short coils we have also the alternative series given in (18). We find then

$$L = 2\pi a N^{2} \left[ 2 \left\{ 1 + \frac{1}{8} \left( \frac{h}{a} \right)^{2} - \frac{1}{64} \left( \frac{h}{a} \right)^{4} \right\} \log_{e} \frac{4a}{h} - 1 + \frac{1}{16} \left( \frac{h}{a} \right)^{2} + \frac{1}{48} \left( \frac{h}{a} \right)^{4} \right]. \quad (32)$$

By using an expression for L in terms of elliptic integrals and expanding, Coffin \* has obtained a series for L with which (32) agrees; Coffin's series was evaluated up to terms in  $(h/a)^*$ . Instead of using one such complicated series, it seems that the two series (31) and (32) should cover between them all the cases that occur in practice.

## XXXIII. Effect of a Prism on Newton's Rings. By Lord Rayleigh, O.M., Pres.R.S.†

WHEN Newton's rings are regarded through a prism (or grating) several interesting features present themselves, and are described in the "Opticks." Not only are rings or arcs seen at unusual thicknesses, but a much enhanced number of them are visible, owing to approximate achromatism-at least on one side of the centre. The first part of the phenomenon was understood by Newton, and the explanation easily follows from the consideration of the case of a true wedge, viz. a plate bounded by plane and flat surfaces slightly inclined to one another. Without the prism, the systems of bands, each straight parallel and equidistant, corresponding to the various wave-lengths (λ) coincide at the black bar of zero order, formed where the thickness is zero at the line of intersection of the planes. Regarded through a prism of small angle whose refracting edge is parallel to the bands, the various systems no longer coincide at zero order, but by drawing back the prism, it will always be possible so to adjust the effective dispersive power as to bring the nth bars to coincidence for any two assigned colours, and therefore approximately for the entire spectrum.

"In this example the formation of visible rings at unusual thicknesses is easily understood; but it gives no explanation of the increased numbers observed by Newton. The width of the bands for any colour is proportional to  $\lambda$ , as well after the displacement by the prism as before. The manner of

<sup>\*</sup> Coffin, Bulletin of Bureau of Standards, vol. ii. p. 113 (1906). † Communicated by the Author.

overlapping of two systems whose nth bars have been brought to coincidence is unaltered; so that the succession of colours in white light, and the number of perceptible \* bands, is much as usual.

"In order that there may be an achromatic system of bands, it is necessary that the width of the bands near the centre be the same for the various colours. As we have seen, this condition cannot be satisfied when the plate is a true wedge; for then the width for each colour is proportional to  $\lambda$ . If. however, the surfaces bounding the plate be curved, the width for each colour varies at different parts of the plate, and it is possible that the blue bands from one part, when seen through the prism, may fit the red bands from another part of the plate. Of course, when no prism is used, the sequence of colours is the same whether the boundaries of the plate be straight or curved."

In the paper † from which the above extracts are taken, the question was further discussed, and it appeared that the bands formed by cylindrical or spherical surfaces could be made achromatic, so far as small variations of λ are concerned, but only under the condition that there be a finite separation of the surfaces at the place of nearest approach. If a denote the smallest distance, the region of the nth band may form an achromatic system if

$$a = \frac{1}{4} n \lambda. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

At the time pressure of other work prevented my examining the question experimentally. Recently I have returned to it and I propose now to record some observations and also to put the theory into a slightly different form more convenient for comparison with observation.

For the present purpose it suffices to treat the surfaces as cylindrical, so that the thickness is a function of but one coordinate x, measured along the surfaces in the direction of the refraction. The investigation applies also to spherical surfaces if we limit ourselves to to points lying upon that diameter of the circular rings which is parallel to the refraction ‡. If we choose the point of nearest approach as the origin of x, the thickness may be taken to be

$$t = a + bx^2, \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

<sup>\*</sup> Strictly speaking the number of visible bands is doubled, inasmuch as they are now formed on both sides of the achromatic band.

<sup>† &</sup>quot;On Achromatic Interference Bands," Phil. Mag. xxvii. pp. 77, 189,

<sup>1889; &#</sup>x27;Scientific Papers,' iii. p. 313.

† In the paper referred to the general theory of curved achromatic bands is considered at length.

where b depends upon the curvatures. The black of the nth order for wave-length  $\lambda$  occurs when

$$\frac{1}{2}n\lambda = a + bx^2, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or

$$x = \sqrt{\left\{ \left(\frac{1}{2}n\lambda - a\right)/b \right\}}, \quad . \quad . \quad . \quad (4)$$

so that

$$\frac{dx}{d\lambda} = \frac{\frac{1}{4}n}{\sqrt{b \cdot \sqrt{(\frac{1}{2}n\lambda - a)}}}. \quad . \quad . \quad . \quad (5)$$

The *n*th band, formed actually at x, is seen displaced under the action of the prism. The amount of the linear displacement  $(\xi)$  is proportional to the distance D at which the prism is held, so that we may take approximately

$$\frac{d\xi}{d\lambda} = -\beta \cdot D, \quad . \quad . \quad . \quad . \quad (6)$$

 $\beta$  representing the dispersive power of the prism, or grating. The condition that the *n*th band may be achromatic (for small variations of  $\lambda$ ) is accordingly

$$\frac{d(x+\xi)}{d\lambda} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

or

a quadratic in n. The roots of the quadratic are real, if

$$\beta^2 D^2 b > a/\lambda^2. \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (9)$$

If a be zero, the condition (9) is satisfied for all values of D, so that at whatever distance the prism be held there is always an achromatic band. And if a be finite, the condition can still always be satisfied if the prism be drawn back far enough.

From (8) if  $n_1$ ,  $n_2$  be the roots,

$$\frac{1}{n_1} + \frac{1}{n_2} = \frac{\lambda}{2a}$$
. (10)

Again, if a=0, that is if the plates be in contact,  $n_1=0$ , and

$$n_2 = 8\lambda \beta^2 D^2 b. \dots (11)$$

The order of the achromatic band increases with the dispersive power of the prism and with the distance at which it is held. The corresponding value of x from (4) is

$$x = 2\lambda \beta D. \qquad . \qquad . \qquad . \qquad . \qquad (12)$$

If a be finite, there is no achromatic band so long as D is less than the value given in (9). When D acquires this value, the roots of the quadratic are equal, and

$$\frac{1}{n_1} = \frac{1}{n_2} = \frac{\lambda}{4a},$$

or

$$n_1 = n_2 = 4a/\lambda.$$
 . . . . (13)

This is the condition formerly found for an achromatic system of bands. If D be appreciably greater than this, two values of n satisfy the condition, viz. there are two separated achromatic bands, though no achromatic system. From (8)

$$n_1 n_2 = 16 a b \beta^2 D^2$$
, . . . . . . (14)

Thus if D be great, one of the roots, say  $n_2$ , becomes great, while the other, see (10), approximates to  $2a/\lambda$ , that is to half the value appropriate to the achromatic system (13).

There is no particular difficulty in following these phenomena experimentally, though perhaps they are not quite so sharply defined as might be expected from the theoretical discussion, probably for a reason which will be alluded to presently. It is desirable to work with rather large and but very slightly curved surfaces. In my experiments the lower plate was an optical "flat" by Dr. Common, about six inches in diameter and blackened behind. The upper plate was wedge-shaped with surfaces which had been intended to be flat but were in fact markedly convex. In order to see the bands well, it is necessary that the luminous background, whether from daylight or lamp-light, be uniform through a certain angle, and yet this angle must not be too large. Otherwise it is impossible to eliminate the light reflected from the upper surface of the upper plate, which to a great extent spoils the effects. In my case it sufficed to use gas-light diffused through a ground-glass plate whose angular area was not so great but that the false light could be thrown to one side in virtue of the angle between the upper and lower surfaces of the wedge \*. It will be understood that these precautions are needed only in order to see the effects at their best. The most ordinary observation and appliances suffice to exhibit the main features.

Another question which I was desirous of taking the opportunity to examine was one often propounded to me by my lamented friend Lord Kelvin, viz. the nature of the

<sup>\*</sup> Compare "Interference Bands and their Applications," Scientific Papers, iv. p. 54.

obstruction usually encountered in trying to bring two surfaces nearly enough together to exhibit the rings of low order. In favour of the view that the obstacle is merely dust and fibres, I remember instancing the ease with which a photographic print, enameled by being allowed to dry in contact with a suitably prepared glass plate, could be brought back into optical contact after partial separation therefrom. My recent observations with the glass plates point entirely in the same direction. However carefully the surfaces are cleaned by washing and wiping—finally with a dry hand, the rings of low order can usually be attained only at certain parts of the surface \*. If we attempt to shift them to another place chosen at random, they usually pass into rings of higher order or disappear altogether. On the other hand, when rings of low order have once been seen at a particular place, it is usually possible to lift the upper glass carefully and to replace it without losing the rings at the place in question. I have repeatedly lifted the glass when the centre of the system was showing the white of the first order or even the darkening (I do not say black) corresponding to a still closer approximation, and found the colour recovered under no greater force than the weight of the Some time is required, doubtless in order that the air may escape, for the complete recovery of the original closeness; but in the absence of foreign matter it appears that there is no other obstacle to an approximation of say  $\frac{1}{8}\lambda$ .

In making the observations it is convenient to introduce a not too small magnifying lens of perhaps 8 inches focus and to throw an image of the source of light upon the pupil of the eye. With the glasses in contact it is easy to trace the rise in the order of the achromatic band as the eye and prism are drawn back. As regards the latter a direct-vision instrument of moderate power (three prisms in all) is the most suitable. An interval between the glasses may be introduced by stages. When the approximation is such as to show colours of the 3rd or 4th orders at the centre, it becomes apparent that the best achromatic effects are attained when the prism is at a certain distance, and that when this distance is exceeded the more achromatic places are separated

<sup>\*</sup> The plates are here supposed to be brought together without sliding. By a careful sliding together of two surfaces, the foreign matter may be extruded, as in Hilger's echelon gratings, where optical contact is attained over considerable areas.

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by a region where the bands are fringed with colour. This feature becomes more distinct as the interval is still further increased, so that without the prism only faint rings or none at all can be perceived. For the greater intervals the interposition of a piece of mica at one edge is convenient. In judging of the degree of achromatism, I found that narrow coloured borders could be recognized as such much more easily by one of my eyes than by the other, and the difference

did not seem to depend on any matter of focussing. In observing bands of rather high order, the question obtruded itself as to whether the achromatism was anywhere complete. It will have been remarked that the theoretical discussion, as hitherto given, relates only to a small range of wave-length and that no account is taken of what in the telescope is called secondary colour. So long as this limitation is observed, the character of the dispersive instrument does not come into play. It appeared, however, not at all unlikely that even with gaslight the range of wave-length included might be too great to allow of this treatment being adequate; and with daylight, of course, the case would be aggravated. It is thus of interest to examine what law of dispersion is best adapted to secure compensation and in particular to compare the operation of a prism and a grating.

As to the law of dispersion to be aimed at, we have from

(4), if  $\lambda = \lambda_0 + \delta \lambda$ ,

$$x = \left\{ \frac{\frac{1}{2}n\lambda_0 - a}{b} \right\}^{\frac{1}{2}} \left\{ 1 + \frac{\frac{1}{4}n\delta\lambda}{\frac{1}{2}n\lambda_0 - a} - \frac{1}{8} \left( \frac{\frac{1}{2}n\delta\lambda}{\frac{1}{2}n\lambda_0 - a} \right)^2 + \dots \right\}$$
 (15)

If  $\xi$  be the displacement due to the instrument,  $\xi$  should be a similar function of  $\delta\lambda$ . In this matter the constant terms (independent of  $\delta\lambda$ ) are of no account, and the terms in  $\delta\lambda$  may be adjusted to one another, as already explained, by suitably choosing the distance D. In pursuing the approximation, what we are concerned with is the ratio of the term in  $(\delta\lambda)^2$  to that in  $\delta\lambda$ . And in (15) this ratio is

$$-\frac{1}{8}\frac{n\delta\lambda}{\frac{1}{2}n\lambda_0-a}; \qquad . \qquad . \qquad (16)$$

thus in the particular cases

$$a = 0,$$
 
$$-\frac{1}{4}\frac{\delta\lambda}{\lambda_0}; \qquad (17)$$

$$a = \frac{1}{4}n\lambda_0, \qquad -\frac{1}{2}\frac{\delta\lambda}{\lambda_0}. \qquad (18)$$

Corresponding expressions are required for the dispersive instruments. In any particular case they could of course be determined; but no very simple rules are available in general. If the intrinsic dispersion be small—the necessary effect being arrived at by increasing D, we may make the comparison more easily. Thus in the case of the grating the variable part of  $\xi$  is proportional to  $\delta\lambda$  simply, so that the ratio of the second and third terms, corresponding to (16), is zero. And in the case of the prism if we assume Cauchy's law of dispersion, viz.  $\mu = A + B\lambda^{-2}$ , we get in correspondence with (16)

$$-\frac{3}{2}\frac{\delta\lambda}{\lambda_0}. \quad . \quad . \quad . \quad . \quad (19)$$

So far as these expressions apply, it appears that the dispersion required is between that of a grating and of a prism, and that especially when a=0 the grating gives the better approximation. It would be possible to combine a grating and a prism in such a way as to secure an intermediate law, the dispersions cooperating although the deviations (in the case of a simple prism) would be in opposite directions.

I have made observations with a grating, using for the purpose a photographic reproduction upon bitumen \*. This contains lines at the rate of 6000 to the inch and gives very brilliant spectra of the first order. I thought that I could observe the superior achromatism of the most nearly achromatic bands as compared with those given by the prism, but the conditions were not very favourable. The dispersive power was so high that the grating had to be held very close, and the multiplicity of spectra was an embarrassment. If it were possible to prepare a grating with not more than 3000 lines to the inch, and yet of such a character that most of the light was thrown into one of the spectra of the first order, it might be worth while to resume the experiment and, as suggested, to try for a more complete achromatism by combining with the grating a suitable prism.

Terling Place, Witham, Jan. 30, 1908.

<sup>\* &#</sup>x27;Nature,' liv. p. 332, 1896; 'Scientific Papers,' iv. p. 226.

## XXXIV. On Mechanical Phosphorescence. By Andrew Stephenson\*.

1. In explanation of the phenomena of phosphorescence it is generally held that the energy communicated by the incident light is stored as potential energy of the molecules, and that on the removal of the light the change of configuration ceases to be stable and the system gradually returns to its initial state, the potential energy setting upvibratory motion, and thereby becoming dissipated as emitted light. The change occurring in the substance during this process is considered to be of such a radical nature as is designated by chemical change.

We propose here to show that a simple type of mechanical system exhibits the chief phenomena of phosphorescence, and furthermore that the agreement between the properties of the phosphorescing substances and those of the system is of

a quantitative nature.

The energy stored by the system under the incident disturbance is kinetic, so that the explanation offered has nothing

in common with that stated above.

It will appear that the argument is general in character, applying to any mechanical system that can be treated by the method of normal coordinates. On account of the gain in vividness, however, it is convenient to make use of a particular system; the main facts forming the basis of the theory are then capable of simple exposition apart from the

analytical development.

2. Consider a particle suspended from a fixed point by a light elastic string; if we regard the system as confined to a vertical plane it is fixed by two coordinates, and the normal motions are the vertical vibration and the horizontal (pendulum) swing. If the system is frictionless—a case which may be considered by way of introduction—the normal motions are in general practically independent; the vertical vibration creates a small periodic change in the spring of the pendulum motion, while the latter exerts a second order forcing disturbance on the former, but neither of these actions is cumulative in effect unless the periods are properly adjusted. When the periods vertically and horizontally are approximately in the ratio 1/2 there is mutual interaction: if the system is initially in vertical motion, any small horizontal swing is gradually magnified through the periodic change of approximately double

<sup>\*</sup> Communicated by the Author.

frequency in its spring\*, while if, on the other hand, the motion is initially horizontal, a vertical vibration is forced by the isochronous variation in the tension. Some notion of the marked nature of this interaction may best be gained from

experimental observation.

Now let us suppose that the vertical coordinate is subject to kinetic friction, while the other is frictionless. Then, whatever the relation between the periods, the pendulum motion forces a small oscillation vertically, in general of second order amplitude, maintaining it against friction; thus the energy is gradually dissipated and the frequency of the emission is double that of the pendulum.

Consider the effect of a periodic disturbance applied radially. In general it will merely produce an isochronous forced vibration vertically, but if the frequency is approximately double that of the pendalum motion, this oscillation will in turn magnify any existing small pendulum swing; thus the system stores energy absorbed from incident disturbance of

the particular frequency.

For a given intensity of disturbance the amount of energy obtained in this way will depend upon the time of action, but

evidently it must have some definite upper limit.

When the exciting force is removed the pendulum motion generates a comparatively small forced oscillation vertically of double its own frequency, which continues until the energy is dissipated against the kinetic friction. Thus the system gives out the stored energy in a definite frequency during an interval which is comparable with, and may indeed be large compared with, the time of action of the incident disturbance. That is, the system phosphoresces.

It is to be noted that in the special case when the frequencies of the normal motions vertically and horizontally are in the ratio 2/1, the forced oscillation vertically under the exciting disturbance, the energy stored, and the subsequent rate of

energy emission have their greatest values.

A disturbance acting on a coordinate through periodic change of spring has a continually cumulative effect when the ratio of its frequency to that of the free motion of the coordinate lies anywhere within a certain range. In the above, therefore, energy is stored under incident force of any period within a range, but the resulting emission is always of one definite frequency, i. e. double that of the free pendulum motion.

<sup>\* &</sup>quot;On a Class of Forced Oscillations," § 2, Quarterly Journal of Mathematics, no. 168 (1906).

The class of phosphorescent substances exhibits exactly

similar phenomena.

The qualitative agreement being thus far established, we proceed to examine the quantitative properties of our typical system\*.

3. If r is the length of the string and  $\theta$  the inclination to the vertical at time t, the equations of motion of our system under

the radial disturbance are

$$r\ddot{\theta} + 2\dot{r}\dot{\theta} + g\theta = 0.$$
 (i.)

$$\ddot{r} + 2 \kappa \dot{r} - r \theta^2 + c^2 (r - l) = an^2 \cos 2nt$$
 . . (ii.)

In the case of a system which receives energy from, or gives up energy to, a surrounding medium the 'frictional' coefficient,  $\kappa$ , may be large during emission and negligible during absorption. Thus in the present case if the suspended body exposes a large surface the effect of periodic disturbance communicated through the air is accounted for by the term on the right of (ii.), and  $\kappa$  represents merely the internal frictional force which may be small: when, on the other hand, the body is giving up energy by the generation of periodic motion in the air,  $\kappa$  is large. We shall therefore assume that  $\kappa$  is zero while the system is storing energy, but is large during emission.

Assuming the amplitude of  $\theta$  to be small initially, we have

$$r = l - 2\alpha \cos 2nt$$
.

where l is the length of the string in equilibrium, and

$$\alpha = \frac{1}{2} \frac{an^2}{4n^2 - c^2}.$$

Putting  $\theta = \phi/r$  we have from (i.)

$$r \ddot{\boldsymbol{\phi}} + (g - \ddot{r}) \boldsymbol{\phi} = 0,$$

$$i.e. \left(1 - \frac{2\alpha}{l}\cos 2nt\right) \ddot{\boldsymbol{\phi}} + \left(\mu^2 - \frac{2\alpha}{l} \cdot 4n^2\cos 2nt\right) \boldsymbol{\phi} = 0, \quad \text{(iii.)}$$

where  $\mu^2 = g/l$ .

<sup>\*</sup> The results of the analysis in § 3-§ 5 are summarised in § 6.

The solution of this equation is of form\*

$$\phi = \sum_{1}^{\infty} \left[ a_{2r-1} \cos \left\{ (p - 2\overline{r-1} \, n)t + \epsilon \right\} + a_{-(2r-1)} \cos \left\{ (p + \overline{2r-1} \, n)t + \epsilon \right\} \right],$$
where  $\epsilon$  is arbitrary. (iv.)

On substitution in (iii.) we find

\* The method is similar to that employed in the paper already quoted; a change of notation is introduced which makes the solution easier to handle for our present purpose, although the simple idea underlying the method is thereby rendered less readily apparent. For the general principle reference may be made to the previous work. The solution is here carried to a higher approximation.

In the limit  $r = \infty$ 

$$\frac{a_{\pm(2r-1)}}{a_{+(2r-3)}} = \frac{\alpha}{l} < 1 \text{ numerically,}$$

so that the series is convergent. The above equations are sufficient to determine p and the a's. Our special object is to find the range of n near  $\mu$  for which p is imaginary; such a value of p indicates a continually increasing amplitude of  $\phi$ , and therefore of  $\theta$ , due to the influence of r. In the general case it is not a practicable matter to obtain the solution of this problem in finite terms, and we shall therefore assume that  $\alpha$  is small. The coefficients then diminish rapidly, and we shall neglect those lying beyond  $a_3$  and  $a_{-3}$ . Then to the required degree of approximation

$$a_{\pm 3} = -\frac{\alpha}{l} \frac{3}{8} a_{\pm 1};$$

and on substituting in (1) and (-1) we have

$$a_1 \left\{ \mu^2 - (p-n)^2 - \frac{15}{8} n^2 \frac{\alpha^2}{l^2} \right\} = \frac{\alpha}{l} \left\{ 4n^2 - (p+n)^2 \right\} a_{-1}$$

$$a_{-1} \left\{ \mu^2 - (p+n)^2 - \frac{15}{8} n^2 \frac{\alpha^2}{l^2} \right\} = \frac{\alpha}{l} \left\{ 4n^2 - (p-n)^2 \right\} a_1,$$

whence

$$\begin{split} \left\{ \mu^2 - (p-n)^2 - \frac{15}{8} n^2 \frac{\alpha^2}{l^2} \right\} \left\{ \mu^2 - (p+n)^2 - \frac{15}{8} n^2 \frac{\alpha^2}{l^2} \right\} \\ = \frac{\alpha^2}{l^2} \left\{ 4n^2 - (p+n)^2 \right\} \left\{ 4n^2 - (p-n)^2 \right\}. \end{split}$$

 $\mu^2 - n^2$  being of order  $\alpha/l$  this equation is correct to the order  $(\alpha/l)^3$  and determines p to the order  $(\alpha/l)^2$ . Putting  $n^2 = \mu^2 \left(1 + k\frac{\alpha}{l}\right)$  and neglecting powers of  $\alpha/l$  above the third we find

$$p^{2} = -\mu^{2} \frac{\alpha^{2}}{l^{2}} \frac{9 - k^{2} + \frac{57}{4} k \frac{\alpha}{l}}{4 + 2k \frac{\alpha}{l}}.$$

Thus p is imaginary if k lies between the limits  $\pm 3 + \frac{57 \alpha}{8 l}$ , and therefore for a cumulative influence on the  $\theta$  motion  $n^2$ 

must lie within the range between

$$\mu^2 \left(1 \pm 3 \frac{\alpha}{l} + \frac{57}{8} \frac{\alpha^2}{l^2}\right).$$

Also  $-p^2$  is maximum when  $k = \frac{39}{8} \frac{\alpha}{l}$ ; i.e. when

$$n^2 = \mu^2 \left(1 + \frac{39}{8} \frac{\alpha^2}{l^2}\right)$$

and gradually diminishes to zero on either side towards the

ends of the range.

If  $an^2$ , the amplitude of the forcing disturbance, is kept constant, the magnitude of  $\alpha$  depends upon the position of n within the range. By taking c greater than 2n we ensure that  $|\alpha|$  increases along with n, the variation being marked if c-2n is small.

It appears, then, that the system stores energy under incident disturbance of any frequency within a certain range the central value of which is greater than double the frequency of the pendulum motion; and as the intensity of the disturbance increases the range becomes wider and the central value slowly greater.

4. Expressed in real form the equation (iv.) becomes

$$r\theta = Ae^{+ip+t}\sin(nt+\beta) + Be^{-+ip+t}\sin(nt-\beta) + \dots,$$
where
$$\tan \beta = +\sqrt{\frac{3-k}{3+k}},$$

the terms of the first approximation only being retained.

A and B depend upon the initial conditions, but if A is not zero initially the motion tends to the steady phase given by

$$r\theta = Ae^{|ip|t}\sin(nt + \beta),$$

in which the passage of energy to the  $\theta$  coordinate is maximum. If the initial  $\theta$  is sufficiently small this state may be closely approximated to before much of the total energy is stored.

To find what happens after the initial stage we must now consider the reaction of  $\theta$  upon r. Through the term  $r\dot{\theta}^2$  in (ii.) a direct disturbance is applied to the r motion, and this gradually reduces  $2\alpha$ , the amplitude of r, until  $n^2 = \mu^2 \left(1 \pm 3\frac{\alpha}{l} + \frac{57}{8}\frac{\alpha^2}{l^2}\right)$ ; i. e., until n is on the verge of the range of frequency within which magnification takes place.

The effect of the r motion on  $\theta$  is then merely to keep the latter in a forced vibration of constant amplitude, and the system is therefore in the steady state, no further energy being absorbed. It may be noted that when  $n=\mu$  for the steady motion  $\alpha=0$ : in this case of exactly double frequency it is evident without analysis that at a certain amplitude of swing, if the phase is properly adjusted, the periodic variation in tension is exactly balanced by the radial incident disturbance, so that r remains constant and all the incident energy is reflected.

It is of interest to inquire how the amount of energy required for saturation depends upon the intensity of the disturbance and its frequency within the necessary range.

When the system is saturated,

$$k = \mp 3$$
,  $\alpha/l = \mp \frac{1}{3} \left( \frac{n^2}{\mu^2} - 1 \right)$ ,

and  $\beta = 90^{\circ}$  or  $0^{\circ}$  respectively, so that

$$\theta = b_{\sin}^{\cos} nt$$
.

The signs and the phase of  $\theta$  depend upon the sign of  $\alpha_0$ , the initial value of  $\alpha$ . There is no loss of generality in the choice of  $\alpha$  so that  $\alpha_0$  is positive. Then as the  $\dot{\theta}$  swing increases  $\alpha$  is gradually diminished from  $\alpha_0$  to the steady value, which is therefore positive also. Hence in the above equations for  $\alpha/l$ , k, and  $\theta$  the upper or lower values are to be taken according as  $n^2$  is less or greater than  $\mu^2$ .

By substitution in (ii.)

$$\begin{split} \mp \frac{8}{3} n^2 \left( \frac{n^2}{\mu^2} - 1 \right) l \cos 2nt - \frac{1}{2} l b^2 n^2 (1 \mp \cos 2nt) \\ + c^2 \left\{ \pm \frac{2}{3} \left( \frac{n^2}{\mu^2} - 1 \right) l \cos 2nt + \lambda \right\} = a n^2 \cos 2nt, \end{split}$$

where  $\lambda$  is the change in the mean value of r due to the  $\theta$  motion. The terms in  $\left(\frac{n^2}{\mu^2}-1\right)^2$  being of the second order are neglected. We have then

$$\lambda = \frac{1}{2} lb^2 n^2/c^2$$

and

$$\pm b^2 n^2 = \frac{1}{l} \left\{ 2an^2 \mp \frac{4}{3} (c^2 - 4n^2) \left( \frac{n^2}{\mu^2} - 1 \right) l \right\}. \quad (v.)$$

The effect of the increase,  $\lambda$ , in the mean value of r is to

diminish  $\mu^2$ ; and if this is appreciable the frequency of emission after the removal of the incident disturbance must gradually become greater as the energy is given out.

Again, 
$$\frac{n^2}{\mu^2} - 1 = \sigma^2 \frac{\alpha_0}{l}, \text{ where } \sigma^2 < 3.$$

$$= \sigma^2 \frac{1}{2l} \frac{an^2}{4n^2 - c^2},$$

: from (v.) 
$$\pm b^2 = \frac{2}{l} (1 - \frac{1}{3}\sigma^2)a$$
, . . . (vi.)

according as n is less or greater than  $\mu$ , Now if c > 2n, a is negative when  $\alpha_0$  is positive, and therefore the above equation gives  $b^2$  positive if n greater than  $\mu$ , but negative if n less than  $\mu$ . It follows that in the latter case there cannot be steady motion and the amplitude of the  $\theta$  coordinate oscillates periodically. In the steady motion which holds for the upper half of the range it is evident-from (vi.) that the total store of energy necessary for saturation is proportional to the square root of the incident intensity, and gradually decreases to zero as the applied frequency is taken greater within the range. It is to be noted that in the deduction of (vi.) only the terms of the first approximation were retained.

5. When the exciting disturbance is removed the  $\theta$  swing directly forces a small oscillation vertically of exactly half its own period, the energy being thereby dissipated against the kinetic resistance of the vertical coordinate. It is necessary to obtain the conditions under which the emission is of constant frequency throughout its decay. Evidently from the preceding  $\lambda$  must be small compared with  $\alpha_0^2$ ; and on substitution for  $b^2$  in the value of  $\hat{\lambda}$  we find that this is brought about by taking c sufficiently close to 2n. Furthermore, during emission there is motional resistance to the rcoordinate, and by making this large we bring  $\beta$  towards the limit  $\pi/4$ , and therefore cause the frequencies of  $\theta$  and r to approach the limits  $\mu$  and  $2\mu$  respectively to any required degree of approximation. Thus the variation in the phosphorescence frequency during decay is brought within any assigned range however small.

We now seek to express the rate of emission of energy as a function of the time that has elapsed since the removal of

the applied force.

The forced motion of r due to  $\theta$  is of amplitude proportional to the square of the  $\theta$  amplitude, and the work done per oscillation against the motional resistance is therefore

proportional to the fourth power of the swing. Hence, if E is the energy of the  $\theta$  motion at time t,

$$\frac{d\mathbf{E}}{dt} = -q\mathbf{E}^2,$$

where q a constant. This gives

$$\mathbf{E} = \frac{1}{\mathbf{C} + qt},$$

where  $C=1/E_0$ ; therefore

$$\frac{d\mathbf{E}}{dt} = -\frac{q}{(\mathbf{C} + qt)^2}.$$

Now I, the intensity of the phosphorescence, is equal to the rate of energy emission; thus

$$I^{-\frac{1}{2}} = q^{-\frac{1}{2}}(C + qt),$$

i.e., the reciprocal of the square root of the emission intensity

has a uniform time gradient.

The initial intensity is proportional to the square of the total store, and therefore increases proportionally with the incident intensity until the latter becomes so large that our approximation (vi.) does not apply.

6. It may be well now to summarise the properties of the system as regards phosphorescence in the probable order of

their appearance to an experimental observer:—

1. The emission frequency is independent of the exciting disturbance.

2. The system stores energy under incident disturbance of any frequency within a certain range which includes the emission frequency; the greater the intensity of disturbance the greater the range and the greater the excess of its central value above the emission

frequency.

3. For different frequencies within the range the initial rate of energy storage is maximum near the centre, and decreases gradually towards each end. If the frequency of the storing coordinate is less than half the frequency of the other, the system ultimately reaches a steady state only for that part of the range which lies above the emission frequency. In the steady state the energy stored is proportional to the square root of the incident intensity, and it also varies with the applied frequency, gradually decreasing to zero as the latter is taken greater within the range.

4. The reciprocal of the square root of the emission intensity has a uniform time gradient.

5. When the system is saturated the initial emission intensity is proportional to the intensity of the incident disturbance when the latter is small.

## 7. Now when a substance phosphoresces:—

 The emission spectrum in any neighbourhood is independent of the exciting light.

2. Phosphorescence is produced by light of any frequency within a range which includes the emission frequency near its lower end.

3. The intensity of emission is maximum for an exciting frequency greater than that of the emission.

4. The reciprocal of the square root of the emission intensity when plotted against the time, gives a straight line during an interval in which the greater portion (over 90 per cent.) of the stored energy is dissipated; there is then a rapid bend in the graph which quickly becomes straight again at a smaller inclination.

5. The energy stored under given disturbance increases asymptotically to a definite limit, and when the system is saturated the initial emission intensity is proportional to the intensity of the exciting light, provided the latter is not too large \*.

There is thus a remarkable agreement between the properties of the phosphorescent substance and those of the system—an agreement which is all the more striking in view of a very noteworthy difference, namely, that phosphorescent matter gives a band spectrum while the system gives a line. A secondary point of contrast arises in the rate of decay of emission; as we have seen for the system the  $I^{-\frac{1}{2}}-t$  graph is simply a straight line, while in the case of the phosphorescent matter some radical change takes place when only a small percentage of the energy remains, and the rate of change of  $I^{-\frac{1}{2}}$  is diminished. Connected with this there is a hysteresis effect  $\dagger$  which has no analogue in our mechanical system.

The phosphorescent bands differ very much in brilliance

<sup>\* &</sup>quot;On the Decay of Phosphorescence in Sidot-blende and certain other Substances," by Messrs. E. L. Nichols and E. Merritt, Physical Review, vol. xxiii. (1906) p. 37.

<sup>+</sup> Nichols and Merritt, loc. cit.

and duration; in the case of the system these qualities depend on the natural frequency of the coordinate directly acted on by the incident disturbance. If the frequency of this coordinate is equal to that of the emission, it is evident that

maximum intensity in emission is obtained.

8. The simple vapours that give line spectra in fluorescence show no trace of phosphorescence, and it would appear that the band spectrum of phosphorescence is, perhaps, an essential property of the phenomenon. The difference between the system and the phosphorescent substance may thus be fundamental, but the agreement in other respects is of such a nature as to indicate the possibility that in essence there is mechanical identity between the two; that the incident light forces a vibration in a coordinate, which in turn communicates kinetic energy in intensifying vibration in another coordinate until the saturation limit is reached; the reverse process being set up on the removal of the exciting light, with the emission of energy in a frequency double that of the storing coordinate.

The analogue affords marked economy of thought in connecting a number of the chief facts of phosphorescence. It may also be of service in suggesting new directions of experimental examination. We shall conclude with a

reference to two of these.

9. If the spring of a simple oscillation is subject to periodic variation, the amplitude is magnified not only in the case of double frequency, but more generally when the ratio of the natural frequency to that of the disturbance lies anywhere within a range in the vicinity of  $\frac{1}{2}r$ , where r is any integer\*. As r becomes greater the magnifying influence diminishes very rapidly, but when r=2 it is easily observable, although not nearly so pronounced as in the case of double frequency, r=1. Thus if our system is subject to a radial disturbance of frequency nearly equal to that of the pendulum motion, energy will be absorbed, and at once emitted again during the action of the disturbance in approximately double frequency.

It would be of interest to inquire whether phosphorescent substances exhibit a similar phenomenon. As the effect is of the second order, it would be necessary to have the exciting light of great intensity in order to give the matter a fair trial. Experiments to determine the various effects of the infra-red rays have been carried out by Nichols and Merritt

<sup>\*</sup> See the paper already referred to in § 2.

with Sidot blende as phosphorescent substance\*. The waves in this region have the effect of greatly retarding the storage of energy when incident along with the exciting disturbance; and in general they also diminish the total store and rate of emission if applied during phosphorescence. There is an exception to be noted, however, in the case of Sidot blende; one particular band of the phosphorescence spectrum is rendered more intense throughout its decay by application of the infra-red during emission. This effect is consistent with the property enunciated above for the mechanical system, but further experiment is necessary to determine the range of (infra-red) frequency which produces the brightening. If the range were found to contain, or lie near, half the phosphorescence frequency, a further point of resemblance would be established between the mechanical system and the phosphorescent substance.

The general infra-red effects, on the other hand, do not appear to come within the analogue, possibly on account of

the difference referred to in the preceding section.

Another point which is worthy of experimental investigation is the variation in the rate at which energy is stored under given intensity of excitation for different frequencies within the effective range. It has been shown in § 3 that the initial rate of energy absorption in the mechanical system is maximum for a frequency rather greater than the central value of the range, and gradually diminishes towards zero at the ends of the range.

If the excitation intensity is not too great it is found that an appreciable time † is required for the saturation of some phosphorescent substances, and there does not appear to be any insuperable difficulty in the way of the experiment. The inquiry would be of special interest in determining the saturation limit for different frequencies throughout the

range.

Manchester, November 1907.

\* "The Influence of the Red and Infra-red Rays upon the Photoluminescence of Sidot Blende." Physical Review, vol. xxv. (1907)

<sup>+</sup> About five minutes in the only case recorded by Nichols and Merritt, p. 45, in the paper first mentioned. For trustworthy results it would be necessary to make measurements of the *short duration* phosphorescence before the bend of the  $I^{-\frac{1}{2}}-t$  graph.

XXXV. Mutual Induction. By Prof. D. N. MALLIK \*.

If M be the potential energy between any two shells,  $\psi$ ,  $\psi'$  the magnetic strengths of these shells, and  $\omega$  the solid angle subtended at any point of one of the shells by the other, and dn an element of outward drawn normal and ds an element of surface of the first, then we know that

$$\mathbf{M} = \psi \psi' \int \frac{\partial \omega}{\partial n} \, ds.$$

Again, let ds' be the element of surface at any point of the second surface and

 $\rho$  = distance between the points,

dn' =element of outward drawn normal of the second surface.

Then

$$\omega = \int ds' \frac{\partial}{\partial n'} \left(\frac{1}{\rho}\right).$$

$$\therefore \quad \mathbf{M} = \psi \psi' \iint \frac{\partial}{\partial n} \cdot \frac{\partial}{\partial n'} \left(\frac{1}{\rho}\right) ds \cdot ds'.$$

Ex. 1. Two circular wires in any relative position to each other, carrying currents i, i'.

Let  $c_1$ ,  $c_2$  be the radii of the spheres of which they are circular sections, the origin being the centre of both spheres.

Then

$$\begin{split} \mathbf{M} &= -ii' \! \iint \! \frac{\partial}{\partial c_1} \cdot \frac{\partial}{\partial c_2} \frac{1}{\sqrt{c_1^2 + c_2^2 - 2c_1c_2\cos r}} \, ds \cdot ds' \\ &= -ii' \! \int \! \frac{\partial}{\partial c_1} \cdot \frac{\partial}{\partial c_2} \left[ \frac{1}{c_2} \boldsymbol{\Sigma} \left( \frac{c_1}{c_2} \right)^n \mathbf{P}_n(\cos r) \cdot c_1^2 d\mu \, c_2^2 d\mu' \right] d\phi \, d\phi' \\ &= ii' \boldsymbol{\Sigma} \! \int \! n(n+1) \frac{c_1^{n+1}}{c_2^n} \mathbf{P}_n\left(\cos r\right) d\mu \, d\mu' \, d\phi \, d\phi' \; ; \end{split}$$

where  $c_1 > c_2$ ,

 $r= \angle$  between any two radii of the two circles, and  $\mu$ ,  $\phi$  have their usual meanings.

But

$$P_n(\cos r) = P_n(\mu)P_n\cos(r') + \sum T_n^m(\mu)T_n^m(\cos r')\cos m(\phi - \phi'')$$
and

$$P_n(\cos r') = P_n(\mu')P_n(\cos \theta) + \sum T_n^m(\mu')T_n^m(\cos \theta)\cos m(\phi' - \phi'''),$$
\* Communicated by the Author.

where  $\theta = \angle$  between the perpendiculars to the two circles,  $\phi'''$  defining the plane containing these lines,

 $r' = \angle$  between any radius of the second circle and the axis of the first circle  $\phi''$  defining the plane containing these lines.

:. integrating for 
$$\phi$$
 between 0 and  $2\pi$  we have  $\phi'$  . . . . . . . . . . . . .

$$\begin{split} \mathbf{M} &= 4\pi^{2}ii'\Sigma_{n}(n+1) \cdot \frac{c_{1}^{n+1}}{c_{2}^{n}} \mathbf{P}_{n}(\cos\theta) \int \mathbf{P}_{n}(\mu) d\mu \int \mathbf{P}_{n}(\mu') d\mu' \\ &= 4\pi^{2}ii'c_{1}(1-\mu^{2})(1-\mu'^{2})\Sigma \left(\frac{c_{1}}{c_{2}}\right)^{n} \mathbf{P}_{n}(\cos\theta) \frac{d\mathbf{P}_{n}}{d\mu} \cdot \frac{d\mathbf{P}_{n}'}{d\mu'}, \end{split}$$

which is a well-known result.

Ex. 2. Mutual induction between two parallel rectangular wires symmetrically situated and carrying unit currents.

Let x, y, h, and x', y', h', be the coordinates of any two points in the rectangles of which the wires form the contours.

Then 
$$\mathbf{M} = -\frac{\partial}{\partial h} \cdot \frac{\partial}{\partial h'} \int \frac{dx \, dy \, dx' \, dy'}{\sqrt{(x-x')^2 + (y-y')^2 + (h-h')^2}}$$
.

This is directly integrable, for

$$\int \frac{d(x-x')}{\sqrt{(x-x')^2 + \lambda^2}} = \log \left\{ \sqrt{(x-x')^2 + \lambda^2} + (x-x') \right\}, (1)$$
and
$$\int \log \left\{ \sqrt{h^2 + u^2} + u \right\} du$$

$$= u \log \left( \sqrt{h^2 + u^2} + u \right) - \sqrt{h^2 + u^2}. \quad (2)$$

But we may also proceed as follows:-

$$\mathbf{M} = -\frac{\partial}{\partial h} \cdot \frac{\partial}{\partial h'} \int_{a-b}^{a} e^{ax+\beta y} \frac{dx \, dy \, dx' \, dy'}{\sqrt{x'^2 + y'^2 + (h - h')^2}},$$
where  $\alpha \equiv \frac{\partial}{\partial x'}$ ,  $\beta \equiv \frac{\partial}{\partial y'}$ ,
$$= -\frac{\partial}{\partial h} \cdot \frac{\partial}{\partial h'} \int_{a}^{b} \frac{(e^{+\alpha a} - e^{-\alpha a})(e^{+\beta b} - e^{-\beta b})}{\alpha \beta} \frac{dx' \, dy'}{\sqrt{x'^2 + y'^2 + (h - h')^2}}$$

if 2a, 2b are the sides of the first rectangle.

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$$\begin{split} & \stackrel{\cdot \cdot \cdot}{\mathbf{M}} = -\frac{\partial}{\partial h} \cdot \frac{\partial}{\partial h'} \int_{a'}^{a'} \int_{b'}^{b'} 4ab \left( 1 + \frac{a^2}{3!} \left( \frac{\partial}{\partial x'} \right)^2 + \dots \right) \\ & \qquad \left( 1 + \frac{b^2}{3!} \left( \frac{\partial}{\partial y'} \right)^2 + \dots \right) \frac{dx' \, dy'}{\sqrt{x'^2 + y'^2 + (h - h')^2}} \\ & = -16ab \frac{\partial}{\partial h} \cdot \frac{\partial}{\partial h'} \left\{ \sum_{n=0}^{n=\infty} \sum_{m=0}^{m=\infty} \frac{a^{2n} \cdot b^{2m}}{(2n+1)! (2m+1)!} \right\} \\ & \qquad \times \left( \frac{\partial}{\partial a'} \right)^{2n-1} \left( \frac{\partial}{\partial b'} \right)^{(2m-1)} \frac{1}{\sqrt{a'^2 + b'^2 + (h - h')^2}}, \end{split}$$

where

$$\left(\frac{\partial}{\partial a^{l}}\right)^{-1} \frac{1}{\sqrt{a'^{2} + b'^{2} + (h - h')^{2}}} = \int_{0}^{a'} \frac{dx}{\sqrt{x^{2} + b^{2} + (h - h')^{2}}} \&c.,$$

which can be written down from (1) and (2).

If the distance between the planes is small = d,

$$\frac{\partial}{\partial h} \cdot \frac{\partial}{\partial h'} \frac{1}{\sqrt{a'^2 + b'^2 + (h - h')^2}} = \frac{1}{(a'^2 + b'^2 + d^2)^{\frac{1}{2}}}$$
 nearly,

and

$$\begin{split} \mathbf{M} = -16ab \left\{ \Sigma \Sigma \frac{a^{2n} \cdot b^{2m}}{(2n+1)! (2m+1)!} \\ \times \left( \frac{\partial}{\partial a'} \right)^{2n-1} \left( \frac{\partial}{\partial b'} \right)^{2m-1} \frac{1}{(a'^2 + b'^2 + d^2)^{\frac{3}{2}}} \right\}, \end{split}$$

which is directly suitable for calculation if the terms decrease rapidly (the first three terms involving integrals which can be easily evaluated).

The final result can, however, be written down:—For we have

$$\left(\frac{\partial}{\partial a'}\right)^{r} F(a'^{2}) = (2a')^{r} \cdot F^{r}(a'^{2}) + \frac{r(r-1)}{1} (2a')^{r-2} \cdot F^{(r-1)}(a'^{2}) + \dots$$
Put
$$F(a'^{2}) \equiv \frac{1}{\sqrt{a'^{2} + b'^{2} + (h-h')^{2}}} \equiv \frac{1}{\rho} \text{ say};$$
then
$$F^{r}(a'^{2}) = \frac{1 \cdot 3 \cdot (2r-1)}{2^{r}} (-1)^{r} \cdot \frac{1}{\rho^{2r+1}},$$
and
$$\frac{\partial}{\partial r} F(r'^{2}) = \frac{1 \cdot 3 \cdot 5 \cdot (2r-1)}{2^{r}} (-1)^{r} \int_{0}^{r} (a')^{r} r(r-1) \cdot (a')^{r-2}$$

$$\begin{split} \left(\frac{\partial}{\partial a'}\right)^{\mathbf{r}}\mathbf{F}(a'^2) &= \frac{1\cdot 3\cdot 5\cdot (2r-1)}{\rho^{r+1}} \left(-1\right)^r \left\{ \left(\frac{a'}{\rho}\right)^r - \frac{r(r-1)}{2(2r-1)}\cdot \left(\frac{a'}{\rho}\right)^{r-2} + \ldots \right\} \\ &= (-1)^r \cdot \frac{r!}{\rho^{r+1}} \operatorname{Pr}\left(\frac{a'}{\rho}\right). \end{split}$$

Again, if 
$$\begin{split} \mathbf{F}(b'^2) &\equiv \frac{1}{\rho^{r+1}} \mathbf{P}_r \left( \frac{a'}{\rho} \right), \\ \mathbf{F}'(b'^2) &= -\frac{1}{2} \cdot \frac{1}{\rho^{r+3}} \left[ \ (r+1) \, \mathbf{P}_r + \frac{a'}{\rho} \cdot \mathbf{P}_r' \right]; \end{split}$$

but it can be shown that

$$\frac{a'}{\rho} P_{r'} + (r+1) P_{r} = P'_{r+1}.$$

$$\vdots \qquad F'(b'^{2}) = -\frac{1}{2} \cdot \frac{1}{\rho^{r+3}} P'_{r+1},$$
and
$$F''(b'^{2}) = \frac{1}{2^{2}} \cdot \frac{1}{\rho^{r+5}} \left[ (r+3) P'_{r+1} + \frac{a'}{\rho} \cdot P''_{r+1} \right]$$

$$= \frac{1}{2^{2}} \cdot \frac{1}{\rho^{r+5}} P''_{r+2},$$
since
$$\frac{a'}{\rho} P''_{r} + (r+1) P_{r} = P'_{r+1}.$$

$$\vdots \qquad \frac{a'}{\rho} P''_{r+1} + (r+2) P'_{r} = P''_{r+1},$$
or
$$\frac{a'}{\rho} P''_{r+1} + (r+3) P'_{r+1} = P''_{r+2}.$$

$$\vdots \qquad F^{s}(b'^{2}) = (-1)^{s} \frac{1}{2^{s}} \cdot \frac{1}{\rho^{r+2s+1}} P^{s}_{r+s}.$$
where
$$P^{s}(\mu) \equiv \left(\frac{\partial}{\partial \mu}\right)^{s} P(\mu).$$

But

$$\left(\frac{\partial}{\partial b'}\right)^{s} \mathbf{F}(b'^{2}) = (2b')^{s} \cdot \mathbf{F}^{s}(b'^{2}) + \frac{s(s-1)}{1} (2b')^{s-2} \cdot \mathbf{F}^{s-1}(b'^{2}) + \dots$$

$$\begin{split} \left(\frac{\partial}{\partial a'}\right)^{r} \left(\frac{\partial}{\partial b'}\right)^{s} & \left(\frac{1}{\rho}\right) = (-1)^{s+r} r! \left[\frac{b'^{s}}{\rho^{r+2s+1}} P_{r+s}^{s} - \frac{s(s-1)}{1 \cdot 2} \cdot \frac{b'^{s-2}}{\rho^{r+2s-1}} \cdot P_{r+s-1}^{s-1} + \dots\right] \\ & = \frac{(-1)^{s+r} r!}{\rho^{r+s+1}} \left[ \left(\frac{b'}{\rho}\right)^{s} \cdot P_{r+s}^{s} - \frac{s(s-1)}{1 \cdot 2} \cdot \left(\frac{b'}{\rho}\right)^{s-2} P_{r+s-1}^{s-1} + \dots\right]. \end{split}$$

Finally if h-h' is small

$$\frac{\partial}{\partial h} \cdot \frac{\partial}{\partial h'} \left(\frac{1}{\rho^s}\right) = \frac{s}{\rho^{s+2}},$$

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and .:

$$\begin{split} \frac{\partial}{\partial h} \cdot \frac{\partial}{\partial h'} \cdot \left( \frac{1}{\rho^{r+2s+1}} \cdot P^{s}_{r+s} \right) \\ &= \frac{1}{\rho^{r+2s+3}} \cdot P^{s+1}_{r+s+1}, \end{split}$$

and accordingly,

$$\begin{split} \frac{\partial}{\partial h} \cdot \frac{\partial}{\partial h'} \left( \frac{\partial}{\partial a'} \right)^r \cdot \left( \frac{\partial}{\partial b'} \right)^s \frac{1}{\sqrt{a'^2 + b'^2 + (h - h')^2}} \\ = & (-1)^{s+r} \cdot \frac{r!}{\rho^{r+s+3}} \left[ \left( \frac{b'}{\rho} \right)^s \mathbf{P}_{r+s+1}^{s+1} - \frac{s(s-1)}{1 \cdot 2} \left( \frac{b'}{\rho} \right)^{s-2} \mathbf{P}_{r+s}^s + \ldots \right] \cdot \end{split}$$

Ex. 3. Two concentric and coplanar elliptic wires.

Describe coaxial spheroids of which the ellipses are parallel sections.

Then if  $\rho$  is the distance between any two points of the spheroidal shells of which the given ellipses are plane sections,

$$\begin{split} \frac{1}{\rho} &= \frac{1}{h} \Sigma(2n+1) \mathbf{P}_n(\boldsymbol{\mu}) \mathbf{P}_n(\boldsymbol{\mu}') \mathbf{Q}_n(r) \mathbf{Q}_n(r') \\ &+ \frac{1}{h} \Sigma \Sigma 2 \frac{(n-m)!}{(n+m)!} \mathbf{T}_n^m(\boldsymbol{\mu}) \mathbf{T}_n^m(\boldsymbol{\mu}') \mathbf{Q}_n^m(r) \mathbf{Q}_n^m(r') \cos m(\boldsymbol{\phi} - \boldsymbol{\phi}') \end{split}$$

where hr, hr' are the major axes of the elliptic areas,

and

$$\mathbf{M} = -\iint \frac{\partial}{\partial n} \frac{\partial}{\partial n'} \left(\frac{1}{\rho}\right) ds \, ds'.$$

Remembering that  $pdn = h^2 r dr$ ,

and 
$$pds = h^3 r(r^2 - 1) \sin \theta d\theta d\phi$$
  
=  $-h^3 r(r^2 - 1) d\mu d\phi$ ;

we get

$$\begin{split} \mathbf{M} &= -\int h^2(r^2-1)(r'^2-1)d\mu\,d\mu'\,d\phi\,d\phi'\frac{\partial}{\partial r'}\cdot\frac{\partial}{\partial r'}\left(\frac{1}{\rho}\right) \\ &= -h\Sigma(2n+1)(r^2-1)(r'^2-1)\frac{dQ_n}{dr}\cdot\frac{dQ_n'}{dr'}\int \mathbf{P}_n(\mu)\mathbf{P}_n(\mu')\,d\mu\,d\mu'd\phi\,d\phi' \\ &- 2h\Sigma\Sigma\frac{(n-m)!}{(n+m)!}\cdot(r^2-1)\left(r'^2-1\right)\frac{dQ_n^m}{dr}\cdot\frac{dQ_n'^m}{dr'}\int \mathbf{T}_n^m(\mu)\mathbf{T}_n^m(\mu')d\mu\,d\mu' \\ &\qquad \times\cos m(\phi-\phi')\,d\phi\,d\phi'\;; \end{split}$$

and the limits of  $\phi$ ,  $\phi'$  are 0 to  $\pi$ , and those of  $\mu$ ,  $\mu'$  are 1 to 0 taken twice over.

$$\begin{split} \therefore \ \ \mathbf{M} = & - 4\pi^2 h \Sigma \frac{2n+1}{n^2(n+1)^2} (r^2-1) (r'^2-1) \frac{dQ_n}{dr} \cdot \frac{dQ_n'}{dr'} \Big( \frac{d\mathbf{P}_n}{d\mu} \Big)_{\mu=0} \Big( \frac{d\mathbf{P}_{n'}}{d\mu'} \Big)_{\mu'=0} \\ & - 8h \Sigma \Sigma \frac{(n-m)!}{(n+m)!} (r^2-1) (r'^2-1) \frac{(1-\cos m\pi)}{m^2} \frac{dQ_n''}{dr} \cdot \frac{dQ_n''}{dr'} \\ & \times \int \mathbf{T}_n''(\mu) \mathbf{T}_n'''(\mu') \ d\mu \ d\mu'. \end{split}$$

We proceed now to evaluate  $\int_{1}^{0} \mathbf{T}_{n}^{m}(\mu) d\mu$ .

We have

$$\int (1-\mu^2)^{\frac{m}{2}} \frac{d^m P_n}{d\mu^m} d\mu = \frac{d^{m-1} P_n}{d\mu^{m-1}} \cdot (1-\mu^2)^{\frac{m}{2}} + m \int \mu (1-\mu^2)^{\frac{m}{2}-1} \cdot \frac{d^{m-1} P_n}{d\mu^{m-1}} d\mu. \quad (1)$$
at 
$$\mu \frac{dP_n}{d\mu} - \frac{dP_{n-1}}{d\mu} = n P_n.$$

But

 $\therefore$  differentiating m-2 times

$$\mu \frac{d^{m-1}P_n}{d\mu^{m-1}} + (m-2) \frac{d^{m-2}P_n}{d\mu^{m-2}} - \frac{d^{m-1}P_{n-1}}{d\mu^{m-1}} = n \frac{d^{m-2}P_n}{d\mu^{m-2}}.$$
 (2)

Now writing

$$\frac{d^{m-1}\mathbf{P}_n}{d\boldsymbol{\mu}^{m-1}} \equiv \mathbf{D}_{m-1}^n,$$

(2) becomes

$$\mu \mathbf{D}_{m-1}^{n} = \mathbf{D}_{m-1}^{n-1} + (n-m+2) \mathbf{D}_{m-2}^{n}$$
 . . (3)

:. from (1) and (3) we have

$$\int (1-\mu^2)^{\frac{m}{2}} D_m^n d\mu = (1-\mu^2)^{\frac{m}{2}} D_{m-1}^n + m \int (1-\mu^2)^{\frac{m}{2}-1} \left[ D_{m-1}^{n-1} + (n-\overline{m-2}) D_{m-2}^n \right] d\mu \quad . \tag{4}$$

Again,

$$(1-\mu^2)\frac{d\mathbf{P}_n}{d\mu} = n\mathbf{P}_{n-1} - n\mu\mathbf{P}_n.$$

Differentiating m-1 times

$$(1-\mu^{2})D_{m}^{n} - (m-1)2\mu D_{m-1}^{n} - \frac{2(m-1)(m-2)}{2!}D_{m-2}^{n}$$

$$= nD_{m-1}^{n-1} - n\mu D_{m-1}^{n} - (m-1)nD_{m-2}^{n};$$

2.0.

$$(1-\mu^2)D_m^n = nD_{m-1}^{n-1} + \mu(2m-2-n)D_{m-1}^n + (m-1)(m-2-n)D_{m-2}^n.$$
 (5)

.. from (3) and (5) we get

$$\int (1-\mu^{2})^{\frac{m}{2}} D_{m}^{n} d\mu$$

$$= \int (1-\mu^{2})^{\frac{m}{2}-1} \left[ n D_{m-1}^{n-1} + (2m-2-n) \left\{ D_{m-1}^{n-1} + (n-m+2) D_{m-1}^{n} \right\} + (m-1)(m-2-n) D_{m-2}^{n} \right]. \qquad (6)$$

Multiplying (4) by (2m-2) and (6) by m and subtracting, we get

$$(m-2)\int (1-\mu^2)^{\frac{m}{2}} D_m^n d\mu = 2(m-1)(1-\mu^2)^{\frac{m}{2}} D_{m-1}^n$$

$$+ m(n+m-1)(n-m+2)\int (1-\mu^2)^{\frac{m}{2}-1} D_{m-2}^n d\mu$$

$$i.e. \int T_n^m d\mu = \frac{2(m-1)}{m-2} (1-\mu^2)^{\frac{m}{2}} D_{m-1}^n$$

$$+ m \frac{(n+m-1)(n-m+2)}{m-2} \int T_n^{m-2} d\mu,$$
and
$$\int T_n^0 d\mu = \int P_n d\mu$$

$$\int T_n' d\mu = \int (1-\mu^2)^{\frac{1}{2}} \cdot \frac{dP_n}{d\mu}$$

 $= \frac{n}{n+1} \Pi_n \qquad (Phil. Mag. Oct. 1907).$ 

We accordingly have
$$\int_{1}^{1} \mathbf{T}_{m}^{n} d\mu = \frac{2(m-1)}{m-2} \mathbf{D}_{m-1}^{n}(0) + 2m \frac{(n+m-1)(n-m+2)}{(m-2)} \cdot \frac{m-3}{m-4} \mathbf{D}_{m-3}^{n}(0)$$

 $+\dots$ In order to evaluate  $D_{m-1}^n(0)$  &c., we proceed as follows:—

Let 
$$y = \frac{1}{\sqrt{1 - 2\mu k + k^2}} = \sum k^n P_n.$$
Then 
$$\frac{1}{y^2} = (1 - 2\mu k + k^2)$$
or 
$$\frac{dy}{d\mu} = ky^3$$
and 
$$\frac{d^r y}{d\mu^r} = \sum k^n \frac{d^r P_n}{d\mu^r}.$$

$$= 3.5...(2r - 1)k^r . (1 - 2\mu k + k^2)^{-\frac{2r + 1}{2}}:$$

$$\begin{array}{l} \ddots \left(\frac{d^{r}\mathbf{P}_{n}}{d\mu^{r}}\right)_{\mu=0} = \text{coefficient of } k^{n} \text{ in the expansion of} \\ 3.5...(2r-1)k^{r}(1+k^{2})^{-\frac{2r+1}{2}}, \\ \\ \text{or } \mathbf{D}_{r}^{n}(0) = 3.5...(2r-1) \left\{ \frac{(2r+1)(2r+3)...(r+n-1)}{2^{\frac{n-r}{2}}} \left(-1\right)^{\frac{n-r}{2}} \right\} \\ = \frac{1}{2^{n-1}} \frac{(r+n-1)!}{\left(\frac{r+n-1}{2}\right)!} \frac{(-1)^{\frac{n-r}{2}}}{\left(\frac{n-r}{2}\right)!} \\ i. e. \\ \int_{1}^{0} \mathbf{T}_{n}^{m} d\mu = \frac{(-1)^{\frac{n-m+1}{2}}}{2^{n-2}} \left[ \frac{m-1}{m-2} \frac{(n+m-2)!}{\left(\frac{n+m-3}{2}\right)!} \frac{(n-m+1)!}{2^{n-2}} \right] \\ + m \frac{(n+m-1)(n-m+2)}{m-2} \cdot \frac{m-3}{m-4} \frac{(n+m-4)!}{n+m-5!} \frac{n-m+3}{2} . \end{array}$$

$$= \frac{(-1)^{\frac{n-m+1}{2}}}{(m-1)2^{m-2} \cdot n + m - 3!} \frac{(n+m-2)!}{\frac{n-m+1}{2}!} \left\{ (m-1) + m \frac{m-3}{m-4} [n^2 - (m-1)^2] \frac{n-m-2}{n+m-2} + \dots \right\}$$

$$= t_n^m(\mathbf{say})$$

where n-m+1 must be even; otherwise the integral is equal to zero.

Also 
$$\left(\frac{dP_n}{d\mu}\right)_{\mu=0} = 0$$
, if  $n$  is even
$$= (-1)^{\frac{n-1}{2}} \frac{1}{2^{n-1}} \frac{n!}{\left\{\left(\frac{n-1}{2}\right)!\right\}^2} \quad \text{if } n \text{ is odd.}$$

Hence, ultimately,

$$\begin{split} \mathbf{M} &= -4\pi^2 h(r^2-1)(r'^2-1) \sum_{0}^{\infty} \frac{4p+3}{(2p+1)^2(2p+2)^2} \cdot \frac{dQ_{2p+1}}{dr} \cdot \frac{dQ'_{2p+1}}{dr'} \frac{\{(2p+1)\,!\}^2}{2^{4p}(_{f'}\,!)^4} \\ &- \mathbf{16} h \, \mathbf{\Sigma} \mathbf{\Sigma} \frac{(n-m)\,!}{(n+m)\,!} \cdot \frac{(r^2-1)(r'^2-1)}{m^2} \cdot \frac{dQ^m_n}{dr} \cdot \frac{dQ^m_n}{dr'} \cdot t^m_n \, t^{'m}_n, \end{split}$$

where m must be odd, and n must be even.

4. If the ellipses are parallel, with the line joining the centres perpendicular to their planes, the same investigation will apply, only the limits of integration for  $\phi$ ,  $\phi'$ ,  $\mu$ ,  $\mu'$  will be different.

XXXVI. On the Canal-Ray Group. By E. Goldstein\*.

T is permissible to speak of a "canal-ray group," in so far as there exist—as will be shown—several forms of radiation which have certain characteristic features in common with each other and with the canal rays properly so called, while in other respects they exhibit differences of behaviour. By true canal rays we mean those which arise on the side away from the anode, at a cathode completely filling the opening of the tube and provided with small perforations or narrow slits, and which in the case of holes form narrow cones, and in the case of slits beams of slight divergence. Although it is to be surmised that eventually it will be found possible to consider the various members of this group of radiations from a common standpoint, and to reduce their differences to a quantitative gradation, I am nevertheless of opinion that, in the interests of further investigation, it is advantageous, in describing the various members, not to group them together as yet, but to bear in mind their differences as well as their similarities.

The true canal rays on leaving the cathode openings proceed in straight lines, and, in the case of a cathode completely filling the tube, towards the side away from the anode; they are not appreciably deflected by weak magnetic or electrostatic fields. In the case of a plane parallel plate, perforated with a number of holes or slits, the various pencils in general converge towards each other and towards the axis of the plate. Their colour is rosy in hydrogen, bluish in air or nitrogen†. At the glass wall, and in general in any compounds containing sodium, they excite golden-yellow light; in compounds containing lithium the excited light is red, and in magnesium compounds green. In all these cases, the line spectrum of the metal is observed.

Closely allied to the canal rays proper are the rays which

\* Communicated by the Author from the Verhandl. d. Deutsch. Physik.

Gesellsch. iv. p. 228 (1902).
[Note, Jan. 30th, 1908.]—I am greatly indebted to the Editors of the Philosophical Magazine for reprinting the above paper which was published first in the Verhandl. d. Deutsch. Physik. Gesellsch. nearly six years ago. It contains a condensed summary of many years' observations concerning canal rays since my first publication (1886) on this subject. As far as may be judged from recent literature, my observations do not appear to have been of much use hitherto. I would consider it an advantage if the above reproduction would prove to the reader that canal rays are a much more complicated phenomenon than generally admitted.—E. G.

† The common impression that canal rays are golden-yellow in air is based on the effect produced by a form of radiation discussed below.

may be observed in the case of perforated or entire cathodes when the ordinary cathode rays are deflected to one side by a magnet. They spread, in the case of a cathode which completely fills the opening of the tube, not backwards, but towards the anode. Towards magnets and electrostatic fields they are not more sensitive than the true canal rays. hydrogen they appear rosy, in air golden-yellow (cf. below). They excite luminescence in sodium, lithium, and magnesium. Like the canal rays, they are propagated in straight lines, but in the case of a plane plate form a moderately divergent pencil, and in general closely follow the direction of the ordinary cathode rays which start from the same surface and are not influenced by external forces. Their direction relatively to the cathode, as well as the side towards which they are propagated, is indicated by the shape and position of the shadows cast by solids placed in their path\*. In what follows they are briefly termed  $K_1$ -rays  $\dagger$ .

The first layer of the cathode glow, whose behaviour I have recently described in detail ‡, exhibits similarities and close relationship with the canal rays, so much so that one might be led to suppose that the canal rays are identical with the first layer of the cathode glow, and are merely that portion of it which passes unaltered through the openings in

the cathode.

Contrary to this supposition, it has been found \ that the first layer consists of rays which are extraordinarily susceptible to influences that affect canal rays but slightly. This seems to exclude the possibility of a complete identity of the two. The rays of the first layer will be referred to in what follows as  $S_1$ -rays.

\* E. Goldstein, Verhandl. d. Deutschen Physik. Gesellsch. iii. p. 207 (1901).

† [Note, Jan. 30th, 1908.]—The K<sub>1</sub>-rays have first been described in my earliest paper on canal rays (Sitzungsber. d. K. Akad. d. Wissensch. zu Berlin, 1886), where on p. 698 it is shown that rays of the same colour and the same magnetic behaviour as canal rays proper are emitted also by non-perforated cathode-disks standing in the free gas-space, and are found in front of the cathode. In 1901 I described the following experiment (Verhandl. d. Deutsch. Physik. Gesellsch. iii. p. 207):—"As cathode in a tube of about 4 cms. width a nickel disk of 5-10 mm. is used and a wire or a glass rod of some millimetres thickness is fixed for casting a shadow. Evacuating the (hydrogen) gas to a proper degree and bending the ordinary cathodic rays to the side by a magnet, one will observe that the rosy canal-rays form a continuous mass of light filling the width of the tube, while behind the object is lying a sharply-bounded weakly divergent shadow-space. Undoubtedly we see here rays with qualities of canal rays, extending away from the cathode."

‡ E. Goldstein, l. c. iv. p. 64 (1902).

<sup>§</sup> E. Goldstein, l. c. iv. p. 64 et seq. (1902).

The  $S_1$ -rays are also closely related to the  $K_1$ -rays. For if the luminosity of the  $S_1$ -rays is different over different portions of the cathode—a result which may, for example, be produced by the approach of a magnet—the luminosity of the  $K_1$ -rays emitted from the corresponding portions of the cathode surface varies in a similar manner.

There arises the problem of the true origin of the canal

rays.

That the canal rays produced at the back surface of the cathode have their origin at the front surface is rendered very probable by the already established fact \* that the direction of the individual pencils is determined very largely by the shape of the front surface of the cathode, but appears independent of the shape of the back surface. If the latter is plane, e. g., the canal rays are convergent if the front surface is convex, and become divergent if the front surface is made concave.

As regards the origin of the canal rays, it appears to me that the part played by the openings has hitherto not received sufficient attention.

In using slotted plates of not too great a thickness for the production of canal rays, we must regard not so much the entire plates as the walls of the openings—e. g., the opposite sides of a slit—as forming the cathodes; these, along with the edges bounding the openings, are effective in the production of canal rays, and it is incorrect to regard the openings in general as merely forming so many neutral channels of escape.

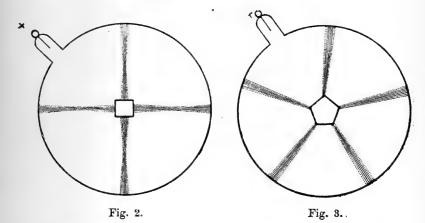
There further seems to me to be a close connexion between the canal rays and a form of radiation which is also obtainable with plane, not perforated cathodes, and which forms rays both tangential to the cathode plane and moderately inclined to it, which pass inwards over the cathode from one of its edges to the opposing edge and then into free space. In the case of a circular plate, these rays obviously only produce a uniform glow around the plate. But if the plate be cut



away in several places along chords (fig. 1), the rays which start from these chords may be recognized—in hydrogen,

<sup>\*</sup> E. Goldstein, Sitzungsber. d. k. Akad. d. Wissensch. zu Berlin, 1886, p. 695; Wied. Ann. lxiv. p. 43 (1898).

e. g., as narrow rosy pencils which pass from the edges lying opposite the chords in a radial direction into space \*. The luminosity of these pencils is comparatively feeble, and hence not easily noticeable; it may, however, be greatly increased by arranging two such congruent cathode plates coaxially at a distance of a few millimetres apart. The luminosity is then not merely doubled, but increased many times. The reasons for this increase of luminosity will be investigated elsewhere. If in a spherical tube (8-11 cms. in diameter) there be fixed facing each other two small congruent squares (side=8 mm.) with their sides parallel, then in (hydrogen) gas at a suitable pressure there may be seen a bright cross (fig. 2) whose luminous arms, of a rosy colour,



proceed from those portions of the space between the two squares corresponding to the middle portions of the sides.

If the cathode consists of a pair of regular pentagons, there is produced a five-rayed star, whose five arms, however, do not arise from the middle points of the sides, but from the angular points of the space between the plates (fig. 3).

In the case of a pair of regular hexagons, there appears a six-rayed star whose rays again appear to arise from the middle points of the sides †. In general, in the case of even-sided regular polygons, the star-shaped figure is formed by

\* E. Goldstein, Physik. Zeitschr. i. p. 133 (1899).

<sup>†</sup> In order to carry out these experiments, we may place two polygonal plates facing each other, and either provide them with separate leading-in wires (attached to their back surfaces or edges), or else make use of a single leading-in wire, the connexion between the two plates being established by means of a thin rod fixed to suitable points.

rays which form continuations of the shortest radii of the polygon, while in the case of odd-sided polygons the rays appear to form continuations of the longest radii. It will be seen that this arrangement is consistent with the supposition that the rays originate from the opposite sides. If the polygons have unequal angles, then in the case of odd-sided figures the pencils may appear at points other than the angular points, and in the case of even-sided figures at points other than the middle points of the sides, but always in a manner consistent with the supposition that they start from the opposite sides.

The rays of these star-shaped figures possess all the properties which may be observed in connexion with true

canal rays.

If the double cathode consists of two congruent rectangles, then a luminous pattern is produced like that shown in fig. 4,

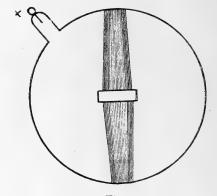


Fig. 4.

which corresponds to a certain pressure of the gas. There arise in the space between the cathodes, from their longer sides, two wide rosy luminous bands, whose initially almost parallel boundaries converge more and more with decreasing pressure of the gas. From the smaller sides there arise two thin pencils of much feebler luminosity, not represented in the figure. The appearance of the two wide bands does not change appreciably if the shorter sides of the plates be connected by plane walls, the cathode then forming a hollow parallelepiped.

If the line of sight be parallel to the long sides of the cathode, the pencils appear in the form of feebly divergent bands, which proceed from the entire width of the space

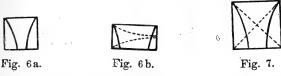
between the plates (fig. 5). A precisely similar appearance is presented by the radial arms of the stars formed when

> using the various double polygons mentioned above, when the line of sight is parallel to the planes of the

polygons.

A more exact knowledge of the path followed by the rays in the space between the plates may be derived from the fact that the rays themselves map out this path on the plates. If a double square has been used for some time as cathode in a gas at suitable pressure, then on stopping the discharge the two opposed plates show a pattern which at first sight appears complicated, but which on closer inspection is seen to consist simply of the superposition of four bands, each arising from a side of the square (fig. 6 a). The bands have a boundary which is concave outwards, and therefore represent a system of rays which gradually narrows as it approaches the opposite side of the square. rosy arm of the cross shown in fig. 2, which issues from the opposite side, is the direct continuation of

the concave band. While the discharge is still in progress it is possible to observe directly that the rosy bands between the plates have the same direction and dimensions as the traces left on the plates when the discharge is arrested.



On the plates of a double rectangle there appears a pattern which is the result of the superposition of two pairs of concave bands, one pair of which is shown in fig. 6 b. Corresponding patterns are obtained with cathode plates of other shapes. The patterns result partly on account of differences in the reflecting power connected with the formation of thin layers of oxide, and partly from shallow grooves produced in the originally plane cathode surface.

From the concave boundary of the traces and of the pencils themselves, it may be inferred that the rays proceeding from any side are subject to an attraction due to the neighbouring We may, for example, imagine that in the case of the square the rays are originally convergent along straight lines, somewhat after the fashion indicated by the dotted lines in fig. 7, and that it is in consequence of the attraction exerted on them by the adjacent sides that they assume the

actually observed form (shown by the full lines). Similar

remarks apply to rectangles &c.

It may be asked in how far all these observations serve to explain the genesis of the canal rays proper. In this connexion it is only necessary to remark that a straight slit in a plane parallel plate represents nothing else than a double rectangle or a hollow parallelepiped, and that a plate with a number of slits forms a system of such double rectangles. Each double rectangle acts like an independent cathode of the same shape, and thus there arises a number of luminous bands similar to those shown for the case of a single double rectangle in fig. 4. If the plate containing the slit completely fills the opening of the tube, only a single luminous band can be produced—viz., that which issues from the edges of the slit on the side towards the anode.

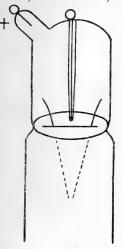
If the perforations of the cathode consist of holes and not of slits, each hole acts like a small hollow cylinder. In the case of a single hollow cylindrical cathode there is produced

a rosy feebly divergent luminous cone.

In the small double rectangles of plates provided with slits, and, mutatis mutandis, in the short hollow cylinders of cathodes perforated with holes, the canal rays pass both tangentially along, and at a moderate inclination to, the inner walls, from the front to the back surface, and into free space. The fact that the rays do not exclusively follow tangential paths explains why even slits a few millimetres in width appear to be completely filled with canal rays, and why each luminous band when viewed in a direction parallel to the shorter side always appears divergent: those rays which are inclined to the walls of the slit and which proceed from opposite walls crossing each other while still in the slit and then passing out in a divergent form. In order to explain details, especially the relatively feeble divergence of the luminous bands, it must be borne in mind that just as the tangential rays are subject to the attraction of the adjacent sides, so also the inclined rays are attracted by the surface of the emitting cathode, and become concave towards it. The rays therefore emerge not along their original directions, but along the tangents to the last elements of the curves which they follow between the walls of the slit.

The fact, on the other hand, that with decreasing pressure of the gas the boundaries of the bands proceeding from the slits become more and more strongly convergent when viewed broadside-on, may be explained by taking into account the relation between the canal rays and the first layer. The canal rays start on the front walls of the narrow double rectangles not only at the places in contact with the first layer, but those rays which pass in a grazing direction over the walls enter the slit along the directions which the rays of the first layer have at the corresponding portions of the edge. Now there appears to apply to the S<sub>1</sub>-rays of a plane cathode a law entirely analogous to that which has long ago\* been established in connexion with the ordinary cathode rays easily deflected by a magnet—viz., that if the pressure be maintained constant, the rays are the more strongly inclined towards the axis of the plate the nearer the starting-point of the rays is to the edge of the plate, and that the less the pressure the more does this inclination of the rays increase. This not only explains why with decreasing pressure the boundaries of the band arising from a slit converge more and more (corresponding to the increasing divergence of the S<sub>1</sub>-rays), but also accounts for the fact that the luminous bands of a system of parallel slits in a plane plate converge towards each other and towards the axis of the plate.

In the case of cathodes which either entirely or nearly fill the opening of the tube, we also have to consider, when working at low pressures, the recently investigated + obliquity of the boundaries of the first layer due, on the one hand, to the repellent anodic action exerted on its base at the cathode, and, on the other, to an attraction of the rays by a cathodic



of place to refer briefly to the effect of very weak magnets on the canal rays. In the case represented in fig. 8, it is possible, by means of a weak and small horseshoe magnet held horizontally—the slit having an equatorial direction—to produce great changes in the directions of the boundaries of the luminous band,

and to render one or other of the boun-

daries very much more oblique.

In this connexion it may not be out

daries (shown dotted in fig. 8).

zone of the wall which lies in the neighbourhood of the outer limit of Crookes's space. If under this influence the extreme S<sub>1</sub>-rays assume the form shown in fig. 8, there results a canal-ray band with very strongly convergent boun-

Fig. 8.

<sup>\*</sup> E. Goldstein, Sitzungsber. d. k. Akad. d. Wissensch. zu Berlin, 1881, p. 799; Wied. Ann. xv. p. 274 (1882).
† E. Goldstein, Verhandl. d. Deutsch. Physik. Gesellsch. iv. p. 64 (1902).

This apparently so powerful effect of a magnet on the direction of the canal rays is primarily conditioned by the change in the direction of the S<sub>1</sub>-rays which results from the approach of the magnet. Yet even this strong effect on the S<sub>1</sub>-rays is not primarily due to the magnet, the primary effect being the magnetic deflexion and distortion of the common cathode rays which excite phosphorescence, and the approach of their extremities towards the cathode. If, for instance, the magnet deflects the rays towards the right hand, then a certain portion of the right-hand wall on which the condensed rays impinge becomes a secondary cathode, which attracts the rays of the first layer, and, by causing them to be attracted towards a region lying nearer the cathode than before, inclines them more towards the right. The consequence is that the right-hand boundary of the convergent canal-ray band becomes inclined even more obliquely upwards and towards the left.—Let it be expressly stated that the possibility, in addition, of a direct effect of the magnet on

the S<sub>1</sub>-rays is not denied.

If a gold wire be arranged as cathode along the axis of a cylindrical tube, then, as is well known, a deposit of gold is produced on the wall around the cathode (in an atmosphere free of oxygen). On replacing the wire by a double square of material (aluminium) which does not disintegrate, with the planes of the squares normal to the axis of the tube, and on producing the cross-shaped system of canal-rays depicted in fig. 2, it is found that after a comparatively short time the thickness of the gold deposit is very materially reduced in the four places where the arms of the cross meet the tube, and ultimately the wall of the tube is in those regions denuded of gold. This property of canal rays may be exhibited in a still more striking and technically more convenient manner by introducing into a tube a double cathode of material subject to disintegration (silver, gold, nickel), in which case those places where the arms of the cross strike the tube remain entirely free from deposit. These regions are in general of a rhombic When they have been mapped out, it is found that on rotating the cathodes about their axis through, say, 45°, the regions formerly free from deposit become covered, while the already covered regions where the rays impinge against the tube become denuded. In general, the particles deposited are transferred from the places where the canal rays have the greatest density to places of lower density \*.

\* [Note, Jan. 30th, 1908.]—Later on Prof. J. J. Thomson (Proc. Cambridge Phil. Soc. xiii. p. 212, 1905) has also observed that canal rays disintegrate metallic surfaces, and the same statement has been made by Mr. Kohlschütter (Zeitschr. f. Elektrochemie, xii. p. 869, 1906).

To a smaller extent, the ordinary cathode rays also possess the property of disintegrating metal surfaces against which they impinge, as I have previously shown \*. Grandquist has pointed out in this connexion that the minimum thickness of deposit occurs where there is a maximum of phosphorescence †. In comparative experiments carried out by myself, the action of the canal rays was markedly stronger. A separation of the two kinds of rays may be effected by means of the strong magnetic deflexion exerted on the ordinary rays which excite phosphorescence.

Connected with this transport of metallic particles are the traces which are left in the canal rays on the cathode surfaces after continued use. Mere differences of colour and reflecting power may already be obtained in a very much shorter time, and, as mentioned above, depend on the formation of layers

of oxide.

The bands and narrow cones of the canal rays are—even in the case of cathodes completely filling the opening of the tube—surrounded by a duller, but very easily noticeable, nebulous light, which fills the entire space even in the case of cylindrical tubes of large cross-section, or spheres 10 cms. in diameter. In order to investigate this light more closely, it is convenient to make use of plate screens completely filling the opening of the tube and provided with only a single slit or hole. It is thus possible to establish the fact that this light contains two forms of radiation. One of these consists —as may be ascertained from the shadows cast by suitable objects—of regular, rectilinear, divergent rays, which proceed from the slit (or hole) in the form of a wide cone, enveloping the canal rays proper. The aperture of the cone exceeded 120° in my experiments. If the S<sub>1</sub>-rays which proceed from a slit viewed end-on be deflected to the right by a magnet, the nebulous rays in the left-hand portion of the tube become brighter. The luminescence of sodium &c. may be excited by these rays just as well as by the canal rays proper. low gaseous pressures, these regular nebulous rays cast deep shadows, which appear quite dark. But with increasing pressure the space corresponding to the shadow becomes gradually filled with the second form of radiation, which consists of diffuse rays. These are produced in a much weaker form in hydrogen than in air (or nitrogen), in which they exhibit a golden-yellow colour.

<sup>\*</sup> E. Goldstein, Thätigkeitsbericht der Phys.-Tech. Reichsanstalt für 1894, p. 70; Zeitschr.f. Instrumentenk. xvi. p. 211 (1897).

† G. Grandquist, Oefvers. Forhandl. Svensk. Akad. 1897, p. 575.

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It seems permissible to suppose that these diffuse rays stand in the same relation to the canal rays proper and to the regular nebulous rays, as does the light of the third layer of the ordinary cathode glow to the regular, ordinary cathode rays—
i. e., that the diffuse rays are due to the impact of the canal rays

proper &c. against the particles of the gas \*.

The diffuse golden-yellow rays play an important part in investigations relating to the canal-ray group. To their existence is due the impression that the canal rays proper themselves emit golden-yellow light. In reality, the light of the canal rays proper is bluish, and it is only the strong diffusion that envelops them in a golden-yellow light which to a large extent obscures the bluish one. To the same cause is to be ascribed the apparently intense chamois to goldenyellow colour of the similarly bluish rays of the first layer in air. It is only at very low pressures, at which diffusion becomes small, that the bluish colour appears more clearly. If by means of an anode fixed in the neighbourhood of the cathode a shadow be produced in the S<sub>1</sub>-rays, this shadow is also, at moderate pressures, not entirely destitute of light, being filled with the diffuse golden-yellow light. This same light also fills the shadow cast in K<sub>1</sub>-rays when the pressure is not very low. It seems that the K<sub>1</sub>-rays, and also the nebulous rays enveloping the canal rays, are bluish in air, and only owe their golden-yellow appearance to the admixture of the diffuse rays.

Even in the case of double cathodes (squares, pentagons, &c.) arranged in free space, a closer investigation shows that the (in hydrogen) rosy arms of the cross- and star-shaped figures form the most prominent, it is true, but not the only kind of rosy light that is related to the canal rays. The bright narrow arms (when viewed in the direction of the axis of the plates) are, as a matter of fact, seen to lie between very feebly illuminated wide fields of rosy light. Shadow-casting objects show that this light is also propagated (away from the cathode) strictly along straight lines, and that it arises from every part of the space between two parallel sides (of the polygonal cathodes), in the form of wide fans—strongly

<sup>\* [</sup>Note, Jan. 30th, 1908.]—In a lately published paper Prof. J. J. Thomson (Phil. Mag. [6] vol. xiv. p. 359, 1907) declares to have "found that positive rays are to be found in all parts of the tube which have an uninterrupted view of the ordinary 'Canalstrahlen,' or of that luminous patch next the cathode of which the Canalstrahlen are the prolongations." Rays of a peculiar intensity are observed by Prof. Thomson "right in front of the cathode."—It seems that my above statements published previously on the diffuse rays and on the  $K_1$ -rays have escaped Prof. Thomson's attention.

divergent in planes parallel to the cathodes—whose rays are also slightly divergent in a plane normal to the cathodes, in a manner similar to that of the star-rays themselves, as shown in fig. 5. The objective existence of the dull fan-shaped pencils of rays which fill up the gaps between the rosy arms of the star may also be shown by using double cathodes of material which undergoes disintegration. It is then observed that, in addition to the regions entirely free from deposit which correspond to the intersections of the bright arms with the walls of the tube, there also appears around the wall a moderately wide zone in which the deposit, though present, is markedly reduced in thickness, as may be seen by transmitted light. In accordance with this, it is also found that in planes which are normal both to the planes and to the sides of the double cathodes, there proceed from the spaces between the plates dull, rectilinear rays, in the form of very wide, divergent, very feeble, wide-angled fans of rays which accompany the moderately divergent and easily seen rays represented in fig. 5. These strongly divergent rays, whose planes of divergence are normal to the plane of symmetry of the double plate, are to be regarded as analogous to the rectilinear nebulous rays mentioned above.

In the formation of the *moderately* divergent pencils shown in fig. 5 there may also take part—in the case of double cathodes—rays which, like the S<sub>1</sub>-rays, appear to proceed from the inner surfaces of the plates, more especially from prominent lines and symmetrically situated points of the polygonal surfaces; in the case of rectangles, e.g., from a portion of the bisecting line parallel to the longer sides. The rays traverse a short distance in a direction nearly normal to the plate, and are then deflected towards it through a large According to the amount of this deflexion, which changes with the pressure, they enclose, together with the rays proceeding from the other plate, spaces of varying shape. Thus at low pressures and with a relatively small deflexion they converge with the corresponding rays of the other plate and form a convergent middle sheet in the outwardly divergent beam of fig. 5. A more detailed account of these very complicated relationships of the rays cannot, however, be given within the limits of a general sketch.

Up to the present, it has been possible to identify (at least) the following members of the canal-ray group:—1. The rays of the first layer. 2. The canal rays proper. 3. The K<sub>1</sub>-rays, which also occur at the front surfaces of continuous (not perforated) cathodes. 4. Regular nebulous rays, which

envelop the canal rays proper. 5. Diffuse rays.

The above list might be extended.

There arises the question as to whether the available material is sufficient to enable us to introduce a guiding and simplifying principle into the study of these complicated phenomena. the literature of the subject, two views have been expressed regarding the nature of the discharge. According to one, the discharge and the radiation effects by which it is accompanied are regarded as a process taking place in the either, the nature of which is not further particularized. According to the other, the discharge and radiation are identified with the motion of charged particles. At the present time the two views would appear to be capable of a certain amount of reconciliation, owing to the fact that many investigators are prepared to abandon the association of ordinary ponderable matter with "electrons," and to regard the masses in question as only apparent. In so far, therefore, as purely electrical processes may be regarded as actions taking place in the ether, a fusion of the two points of view does not appear improbable. champions of the electron theory have gained heuristic aids by expressing the consequences of their hypothesis in mathematical form and attempting to verify the formulæ by experiment. In this connexion it has appeared that in the case of the ordinary cathode rays the following may be regarded as the determining variables:—the potential at which the rays are produced and propagated, the mass of the projected particles, and the magnitude of their charges; the deflectibility of the rays under the action of electric or magnetic fields increasing with the amount of charge, and decreasing with increase of mass and potential.

Possibly from the point of view of the electron theory the required general principle, primarily of heuristic importance, might be established were it possible to determine definitely the as yet doubtful direction of propagation of the  $S_1$ -rays. Should this direction turn out to be—as is often assumed, though without proof—towards the cathode, it would afford a general view-point for certain actions of the canal-ray group. The disintegration of the cathode itself on the one hand, and the removal of the disintegration deposits by the canal rays already described on the other, might then be brought together under the general point of view according to which the  $S_1$ -rays and the canal rays cause removal of the metal wherever they terminate, while in connexion with the spreading of the S<sub>1</sub>-rays in a direction away from the cathode, the rays would produce the same effect at their places of origin as do the canal rays at their terminations. Similar considerations may be applied to the fact that the canal rays excite luminescence in sodium, lithium, and magnesium on encountering these at their terminations, and that a similar luminescence occurs at the surface which forms the base of the S<sub>1</sub>-rays on the cathode. Should the propagation cathode-wards of the S<sub>1</sub>-rays be established, then on the assumption of the already existing hypothesis that the first layer of the cathode glow consists of carriers of positive electricity, we might attempt to deduce the origin of the other members of the canal-ray group of the  $S_1$ -rays. in order to account for the K<sub>1</sub>-rays, we might suppose that during the impact of the positive S<sub>1</sub>-rays on the cathode there occurs a partial rebound of the particles, which are then characterized by a strongly diminished charge, and must therefore in accordance with theory be much less sensitive.— A nearly parallel beam of S<sub>1</sub>-rays arriving in a nearly tangential direction at the walls of a slit would suffer various changes of charge, according to the distance of its individual rays from the cathodic walls of the slit, and would, on account of its variously charged particles being at various distances from, and hence suffering varying deflexions by the negative surfaces, be transformed into a more strongly conical beam, whose components would, in the space between the walls, proceed partly in a tangential, partly in oblique directions. The concavity, towards the neighbouring sides, of the positive beams which sweep across the polygonal plates would thus be accounted for, as well as the fact that outside the space between the plates the rays again proceed along straight lines, forming tangents to the last elements of their curvilinear path between the plates. The decrease of charge taking place during the motion across the plates would explain why the canal rays emerging on the opposite side are much less sensitive than the S<sub>1</sub>-rays. The nebulous rays, which emerge in a highly divergent form, would also be accounted for.

XXXVII. The Radioactivity of Sea-Water. By J. Joly, Sc.D., F.R.S., Professor of Geology and Mineralogy in the University of Dublin, Hon. Sec. Royal Dublin Soviety\*.

AM acquainted with only one determination of the radium in sea-water taken directly from the ocean—that recorded by A. S. Eve in his paper "On the Ionization of the Atmosphere over the Ocean". Strutt had previously determined the radium in sea-salt; and obtained the value

<sup>\*</sup> Communicated by the Author. In part reprinted from the Scientific Proc. Royal Dublin Scc. xi. No. xxii.

<sup>†</sup> Phil. Mag. ser. 6, vol. xiii. p. 248. † Proc. Rov. Soc. vol. lxxviii. p. 151.

 $0.15 \times 10^{-12}$  in grams per gram of salt. This must be reduced, however, to about one-half, seeing that, at the time of this determination, the quantity of radium associated with a gram of uranium was believed to be about double as great as it has since been shown to be—this quantity entering into the calibration of the electroscope. It is necessary to add that Strutt gives his determination as "approximate only."

The sea-water dealt with by Eve was collected in mid-Atlantic, between Montreal and Glasgow. The amount of radium found was  $0.0003 \times 10^{-12}$  gram per gram of sea-water. If we reckon sea-salts as composing 3 per cent. by weight of sea-water, Strutt's determination would give  $0.0023 \times 10^{-12}$ 

gram per gram of sea-water.

Eve also made an experiment on sea-salt, using 400 grams of Omaha sea-salt guaranteed pure by the importers. He finds  $0.02 \times 10^{-12}$  gram per gram, or for the equivalent seawater,  $0.0006 \times 10^{-12}$ .

We thus have the three divergent results:—

From radium in sea-salt (Strutt),  $0.0023 \times 10^{-12}$ . From radium in sea-salt (Eve),  $0.0006 \times 10^{-12}$ . From mid-Atlantic sea-water (Eve),  $0.0003 \times 10^{-12}$ .

In reviewing these figures Eve states that it is safe to conclude that sea-water does not contain more than  $0.0006 \times 10^{-12}$ 

gram radium per gram.

In April of the present year a friend sent me from Valencia, Co. Kerry, a sample of sea-water collected in the harbour at flood-tide. A very large volume of water enters this extensive harbour at each flood; and as there are no large rivers along the coast, water taken at the harbour mouth may be regarded as free from impurities derived from the shore. The quantity sent to me (in a stoppered glass bottle which I had transmitted, specially cleansed, for the purpose) was 2450 c.cs. This was evaporated on the water-bath to about 1200 c.cs., with every precaution against contamination, and in a part of the laboratory in which radioactive preparations had never come. The radium determined in this Valencia sea-water was  $0.0356 \times 10^{-12}$  gram per gram. The apparatus and mode of extraction I was using at this time were closely similar to those developed by Strutt as described in his paper (loc. cit.). The readings of the electroscope were standardized by the emanation from Joachimsthal pitchblende, a portion of which I had analysed for the

This determination, showing more than ten times the

amount of radium given in any evaluation known to me, I

naturally regarded as requiring confirmation.

In the month of May I received from Mr. S. W. Kemp, of the Irish Fishery Department, 2800 c.cs. of sea-water taken in the Irish Channel a few miles to west of the Isle of Man, lat. 53° 53′ N., long. 5° 16′ W. This also was transmitted in bottles which I had supplied for the purpose. The water was evaporated down to about 800 c.cs., and when investigated yielded only  $0.0038 \times 10^{-12}$  gram per gram. This figure seemed to support sea-salt determinations; but I was so convinced of the genuineness of the first result that I provisionally concluded a real difference to exist between near-shore and more open-sea samples of water. I had, indeed, changed the mode of extraction of the emanation, substituting a method in which ebullition proceeds in a partial vacuum, and at its conclusion the space above the liquid in the flask is completely filled with distilled water, thereby securing that every trace of emanation is displaced into a receiver, from which it is transferred into the electroscope. I had found by comparative experiments on known quantities of uraninite in solution, that this mode of extraction gives a somewhat lower constant for the electroscope, showing that it is capable of effecting a more complete extraction. The change in manipulation was therefore in favour of giving a higher, and not lower, result.

Shortly after this measurement, Mr. Kemp sent me three other samples of sea-water. Calling the two samples already

referred to (a) and (b) respectively-

Sample (c) is from lat. 51° 26′ N., long. 12° 5′ W. A point about 65 miles due west of Valencia. Quantity, 2665 c.cs.

Sample (d) is from 1.5 miles south of Crow Head, Co.

Kerry. Quantity, 2740 c.cs.

Sample (e) is from lat. 51° 35′ N., long. 10° 43′ W.—that is, about twenty miles west of Bantry Bay. Quantity, 2764 c.cs. The last two samples were collected on the same day, June 21st.

These were evaporated down as before, each to about 900 or 1000 c.cs. The results were as follows:—

(c)  $0.0126 \times 10^{-12}$ .

(d)  $0.0152 \times 10^{-12}$ .

(e)  $0.0268 \times 10^{-12}$ .

It will be seen that all these figures are of the same order of magnitude as the result on the Valencia water. The discrepancy with the Isle of Man sample is considerable. While

very sure that errors arising from contamination did not enter these results, it seemed probable that some other source of error existed. If this arose from any cause residing in the nature of the material dealt with, it could only be that there was in some way concealment of the emanation in the lower results, and that the higher results were the more nearly approximate to the truth. Sea-water is rich in sulphates; and the possibility of the process of concentration resulting in a precipitation of the radium in non-emanating form occurred to me. There is a small quantity of barium in seawater. A very minute precipitate of this might bring with it the radium; and, again, the calcium sulphate, which is one of the earliest substances to fall, might also be concerned. The emanation, which never increases beyond a certain amount, might be imprisoned in very fine precipitated particles. The flasks were examined with this possibility in view. None of them were perfectly clear of precipitate. In (a) it was least, perhaps; but the dulling of the glass on the inside of the flasks showed that in every case some solid matter had come down. It is true that, in so far as this is redissolved on ebullition, it can do no harm; but the risk of error here was evident.

Accordingly all five were somewhat diluted and transferred to larger flasks, and a few c.cs. of very pure HCl (which I had distilled from a nearly pure acid) added to each. This instantly cleared the precipitates away. They were then boiled and closed. When in due time the whole five came to be redetermined, the results came out as follows:—

(a) Valencia, taken in March,	$0.0400 \times 10^{-12}$ .
(b) Isle of Man, taken in April,	$0.0386 \times 10^{-12}$ .
(c) 65 miles W. of Valencia, June,	$0.0314 \times 10^{-12}$ .
(d) 1.5 miles S. of Crow Head, June,	$0.0226 \times 10^{-12}$ .
(e) 20 miles W. of Bantry Bay, June,	$0.0393 \times 10^{-12}$ .

These, with the exception of (d), are in close agreement; and I find it hard to believe that such a degree of uniformity could arise without a real basis for the results. The deficiency of (d) might originate in a loss of radium in the process of evaporation, the radium being in part left as a precipitate clinging to the evaporating dish. The higher results appear to be the more reliable; indeed, there is the possibility that, in a liquid so rich in sulphates, even these are not a full revelation. I do not regard this, however, as probable.

These results, of course, do not warrant the conclusion that mid-ocean sea-water is equally rich in radium. It might be

that the acid-treatment is effective in bringing into solution

suspended radioactive particles of coastal origin.

It will be evident that measurements made on sea-salts must be unreliable; for there is no assurance that the sample used will contain its due share of the radium which would be carried down among the first constituents precipitated in the preparation of the salt.

Shortly after the above results were communicated to the Royal Dublin Society, five samples of oceanic water collected in the course of a voyage from Madeira to the Bay of Biscay by Dr. F. Stevenson reached me. I will call these f, g, h, i, j, for convenience of reference; giving their place of derivation later on.

Fully realizing the necessity of every precaution, Dr. Stevenson had himself cleansed the vessels in which these waters were transmitted, not only with fresh-water but several times with sea-water, before finally filling up.

As there was sufficient of each sample to enable two determinations to be made, I resolved to vary the procedure

in the several observations.

f. (1) A quantity amounting to 2825 c.cs. was evaporated on the water-bath in my laboratory to 1500 c.cs. and tested without addition of acid. The result was  $0.0029 \times 10^{-12}$ . This was now acidified with 12 c.cs. of pure radium-free HCl, the subsequent examination now gave  $0.0144 \times 10^{-12}$ .

(2) 1650 c.cs. concentrated by evaporation in my laboratory, acidified with 80 c.cs. HCl, closed and examined: result 0.0150 × 10<sup>-12</sup>. Tested a second time the

result was  $0.0213 \times 10^{-12}$ .

g. (1) 2826 c.es. concentrated in my laboratory to 1500 c.es. and acidified with 30 c.es.  $\dot{\text{HCl}}$  gave  $0.0193 \times 10^{-12}$ . Tested a second time, adding 50 c.es.  $\dot{\text{HCl}}$ , result  $0.0273 \times 10^{-12}$ .

(2) 1500 c.cs. not concentrated but directly transferred to the flask, adding 80 c.cs. HCl, afforded 0·0044 × 10<sup>-12</sup>. A second experiment on this gave 0·0080 × 10<sup>-12</sup>.

h. (1) 2500 c.cs. concentrated in the Botanical Laboratory, T.C.D. (a new building in which no radioactive work had been done), with 10 c.cs. HCl gave  $0.0020 \times 10^{-12}$ . Tested again with addition of 50 c.cs. HCl, the reading was  $0.0146 \times 10^{-12}$ .

(2) 1626 c.cs. with 70 c.cs. HCl concentrated in Botanical

Laboratory:  $0.0084 \times 10^{-12}$ .

- i. (1) 1200 c.cs. not concentrated, no acid:  $0.0031 \times 10^{-12}$ . Same with 35 c.cs. HCl:  $0.0260 \times 10^{-12}$ .
  - (2) 1200 c.cs. not concentrated, with 20 c.cs. HCl:  $0.0304 \times 10^{-12}$ .
- j. (1) 1400 c.cs. not concentrated, no acid:  $0.0146 \times 10^{-12}$ . The second lot of j was lost by an accident before its examination.

I give these results with some detail in order that the variations obtained in the readings may be brought out. It is apparent that acid is not always requisite to enable the emanation to be liberated; thus in j the reading is in the second decimal place, although acid was not added. But if there is concentration then acid appears to be requisite, and in some cases a small amount of acid increased to a larger at once raised the amount of emanation obtained. It will be noticed, also, that the second test of any sample invariably affords a higher reading. This is probably due to some effect attending the first boiling, whereby a more perfect solution is obtained. Second tests are on a slightly more dilute solution than first tests, owing to the addition of distilled water in the process of displacing the emanation and gases into the receiver. In the cases of g(2) and h(2) the sea-water, although sufficiently acidified, did not read into the second decimal place, although nearly approaching it. It is to be observed about these two results that the samples of sea-water had stood for nearly two months in the bottles in which they were received, and it is possible that radioactive matter may have settled out or become adherent to the vessels.

Taking the means of those determinations where there had been sufficient acidification, the results stand as follows:—

f. Taken Nov. 4th, 1907; lat. 32° 58′ N., long. 16° 20′ W. (About 70 miles N. of Madeira and 430 from coast of Morocco.)

Radium per c.c.  $0.0169 \times 10^{-12}$  gram.

g. Taken Nov. 5th; lat. 34° 50′ N., long. 15° 19′ W. (About 530 miles west of Strait of Gibraltar and 240 miles from Madeira.)

Radium  $0.0147 \times 10^{-12}$  gram per c.c.

h. Taken Nov. 6th; lat.  $37^{\circ}$  34' N., long.  $13^{\circ}$  56' W. (About 300 miles west of Cape St. Vincent.)

Radium  $0.0115 \times 10^{-12}$  gram per c.c.

i. Taken Nov. 7th; lat.  $40^{\circ}$  39' N., long. 12° 16' W. (About 180 miles west of coast of Portugal.)
Radium  $0.0282 \times 10^{-12}$  gram per c.c.

j. Taken Nov. 8th; lat. 44° 03′ N., long. 10° 21′ W. (About 80 miles north-west of nearest land, at entry of Bay of Biscay.)

Radium  $0.0146 \times 10^{-12}$  gram per c.c. (no acid used).

The mean of these results is  $0.0172 \times 10^{-12}$  and the mean of the maximum results on the five sea-waters is  $0.0217 \times 10^{-12}$ .

More recently still a sample of sea-water reached me from the Arabian Sea. This was collected by my former pupil Mr. R. Friel, of the Indian Civil Service. The bottle used was supplied by me. I concentrated this sea-water immediately on its receipt from its original bulk of 1550 c.cs. to 1000 c.cs., acidifying it with 50 c.cs. of re-distilled HCl, part of which was used in washing out the bottle in which the sea-water travelled. The entire operation was effected in the Botanical Laboratory. The result was:—

k. Sea-water from Arabian Sea, taken Nov. 25th, 1907;
lat. 10° 40′ N., long. 58° 0′ E. (About 400 miles west of Cape Guardafui and 500 miles south of the coast of Arabia):—

Radium per c.c.  $0.0243 \times 10^{-12}$  first experiment. 0.0314 , second , 0.0278 , mean result.

Selecting the result c from the first experiments as derived from a true oceanic water, and accepting the general mean of the five samples of water taken between Madeira and the Bay of Biscay, and finally the mean result on the water from the Arabian Sea, we get a general mean of  $0.0255 \times 10^{-12}$ . Although it is my intention to add to these determinations, and more especially to examine water brought up from ocean depths. it seems allowable to conclude that results so sustained on waters derived from points so far separated, must represent approximately the radium content of oceanic water. Any other assumption seems inconsistent with the fairly uniform composition of sea-water, as regards other constituents, over the world, where special conditions do not intervene to dilute or concentrate it. Eve's result points, indeed, to possible deficiency of radioactive matter in central ocean. My own to some increase near the land. These indications call for further investigation.

As to the validity of the determinations the general agreement among results arrived at, some by concentration, some by direct bottling of the water as it arrived, and again between samples evaporated in the Geological Laboratory and those evaporated in a building only just opened, leaves,

I think, no room to suppose that an unsuspected source of radium contamination can exist. This being so, the principal question arising is whether such measurements truly represent the whole of the radium present. It is indeed remarkable that the quantities of emanation dealt with are by any process capable of extraction from the large volumes of highly saline liquid involved. Thus Ramsay and Soddy\* estimate that the volume of emanation in equilibrium with one gram of radium is but one cubic millimetre; a number closely agreeing with Rutherford's calculated value †. It follows that in about a litre of sea-water there is a maximum of about twenty billionths of a cubic millimetre. That such a minute quantity can be extracted with such an approximate agreement among observations is remarkable. On this point I thought it of interest to see if I could extract with accuracy a known small quantity of emanation generated in the seawater. I accordingly introduced into one of the flasks containing 1400 c.cs. of sea-water, after the determinations were concluded, one milligram of uraninite in solution. A few hours afterwards the sea-water was boiled in the usual manner and the emanation transferred to the electroscope. The yield was almost exactly correct; the small discrepancy (on the side of excess) being no more than a small experimental error would account for. This experiment, indeed, does not prove that after prolonged ebullition there may not remain over a residuum of emanation in sea-water, but it is an assurance as to the reality and meaning of the positive values observed.

It appears to me that the above results go some way towards explaining the difficulty which Eve experienced in accounting for the amount of ionization observed over the ocean (loc. cit.). It must be remembered that over a fluid medium emanation may be derived from considerable distances below the surface, not only by convection currents bringing fresh portions of the medium to the surface, but by the extraction of emanation whenever air becomes mixed up with the water. The process, in the latter case, being in fact the same as that frequently used in extracting emanation from liquids. It seems as if the atmosphere over the ocean might draw upon considerable depths of water for supplies of emanation, whereas over the land the emanating part of the radium must be practically only those atoms at or very near the surface of exposed solids.

Oceanic radioactivity is, most probably, in part referable

<sup>\*</sup> Proc. Roy. Soc. lxxiii. no. 494, p. 346. † 'Nature,' Aug. 20, 1903.

to the denudation of rocks and the transport of the dissolved and suspended radioactive materials to the ocean. The considerable amounts of radium contained in deep-sea sediments, even from the most central parts of the ocean, suggests that much of the uranium reaches the sea in solution or in very fine suspension, and in part ultimately finds a resting-place among the oozes everywhere slowly collecting. On this point I hope shortly to complete my determinations. If this is so, it is improbable that we will ever be in a position to form an equation between the river supply of radium and the oceanic radioactivity.

#### XXXVIII. Notices respecting New Books.

Lehrbuch der Gerichtlichen Chemie. Bearbeitet von Dr. Georg BAUMERT, Dr. M. DENNSTEDT, und Dr. F. VOIGTLÄNDER. Erster Band. Braunschweig: F. Vieweg u. Sohn, 1907. Pp. xvi + 490.

BRIEF notice of the second volume of the new edition of this authoritative work of reference appeared in these columns a few months ago, and the first volume, now before us, completes the work. The nature and classification of poisons are considered in a brief introduction. The work is divided into two parts, a "general" and a "special" one. In the "general" part, an exposition is given of the legal aspect of the subject, and some generalities connected with toxicological analyses are dealt with; the investigation of food-stuffs, utensils, toys, &c. for the detection of poisons is next considered, and finally useful and complete directions are given for the testing and purification of the more important reagents and apparatus used in analyses of this kind. The "special" part, which fills by far the greater part of the volume, deals in detail with the detection of the various poisons. It is divided into three sections. In Section I. are considered inorganic poisons, which are divided into metallic poisons, poisons belonging to the group of the alkaline earths and alkalies, those belonging to the group of acids and the halogens, and, lastly, poisonous gases. Arsenic receives exceptionally full treatment. The section on organic poisons deals with cyanides, carbolic acid, chloroform, alcohol, &c., alkaloids, ptomaines, organic acids and dve-Section III., which is very brief, deals with the conduct of analyses in general. An Appendix contains a brief digest of the various laws relating to poisons. Notwithstanding the fact that the work is primarily addressed to chemists, and that it deals with a subject surrounded with great difficulties, the style is so simple and attractive that a member of the legal profession should have no difficulty in reading it, and in deriving from it information which would prove of great assistance to him in the investigation of criminal cases.

The Polarity of Matter. By Alex. Clark, M.A. London: Gall & Inglis. 1907. Pp. viii+134.

"The atmospheric air is a magnetisable substance."...." When iron filings are placed on a sheet of paper over the poles of a magnet, each fragment forms a small portion of an elliptic curve. These curves do not represent lines of force, as sometimes supposed, but merely the posture in which the particles are carried towards the magnet."...." Electricity, therefore, is merely a modified form of the force inherent in the particles of matter, and is the same force which in other circumstances we call gravitation."...." Having arrived at the parting of the ways, Hertz unfortunately took the wrong turn. Instead of accepting the conclusion that they (Hertzian waves) are heat waves, and endeavouring to account for their magnetising effect, he assumed the identity of electricity and light, which is impossible." Thus our author; and we are left wondering how this book ever came to be published.

Guide de Préparations Organiques à l'Usage des Étudiants. Par E. Fischer. Traduction autorisée d'après la septième édition allemande par H. Decker et G. Dunant. Paris : Gauthier-Villars. 1907. Pp. xviii+110.

This small laboratory guide should prove of great assistance to all students entering on a course of laboratory work in organic chemistry. In the selection of the preparations, the author was guided partly by the price of the necessary materials and apparatus, partly by the time required to carry out the various operations described, and partly by considerations of safety. The author wisely devotes the introductory portion of the work to the precautions to be observed by the experimenter in order that accidents may be avoided. The book is divided into two parts, Part I. being devoted to preparations of importance to professional chemists, and Part II. to compounds which are of special interest to the biologist or medical man. An index of the various compounds dealt with completes this excellent little work.

Die Binokularen Instrumente. Nach Quellen bearbeitet von Moritz von Rohr. Berlin: Julius Springer, 1907. Pp. viii+224.

This monograph deals in a thorough manner with the theory and history of binocular instruments. Its preparation must have involved a great deal of labour and patient study, and the author is to be congratulated on having rendered a very valuable service to manufacturers of binocular instruments and others interested in the subject, by bringing together in a comparatively small volume so much useful information, and more especially by placing before his readers so thorough a survey of the history of the subject. Some idea of the amount of historical research embodied in this volume may be gathered from the bibliography of

the subject given at the end of the book, which extends over nearly 20 pages and contains hundreds of references. A thorough knowledge of the history of a subject such as that dealt with in the present volume is essential to all would-be discoverers and inventors, as it prevents waste of time and—what is perhaps more trying—bitter disappointment at finding that an apparently new invention was well known to an older generation. We can give no higher praise to the volume than by saying that it is fully worthy of its author's reputation, and that the arduous task which he has attempted has been accomplished with all the thoroughness which might have been expected of him.

Annuaire pour l'An 1908. Publié par le Bureau des Longitudes. Avec des Notices scientifiques. Paris : Gauthier-Villars.

This year's issue of the Annuaire contains various physical and chemical tables, and the following special articles:—La distance des astres et en particulier des étoiles fixes, by M. G. Bigourdan; and L'École d'Astronomie pratique de l'Observatoire de Montsouris, by M. E. Guyon.

The Science Year Book and Diary for 1908. Edited by Major B. F. S. BADEN-POWELL.

The fourth issue of this year-book differs but little from its predecessor. The diary part of the book is as before of paper of excellent quality. The "Biographies" section is still very imperfect. We note that Professor Rutherford's address is given as "McGill University, Montreal."

Leçons sur la Viscosité des Liquides et des Gaz. Par Marcel Brillouin, Professeur au Collège de France. Seconde Partie. Viscosité des Gaz. Caractères Généraux des Théories Moléculaires. Paris: Gauthier-Villars. 1907. Pp. 142.

The author commences this concluding volume of a treatise on viscosity by a description of the earlier researches on the viscosity of gases, in which the pendulum and oscillating disk methods were employed. The experiments of O. E. Meyer, Bessel, and Girault are dealt with and criticised. The next chapter is devoted to an account of the researches of Maxwell, Kundt and Warburg; the various forms of apparatus employed by these physicists are illustrated and described very fully. The flow of gas through a cylindrical tube is next dealt with, and an excellent resumé is given of the work of Graham, Meyer, and Warburg. Absolute determinations, the viscosity of gases at high temperatures, and the behaviour of vapours are then considered, while various comparatively recent determinations are described in the last chapter of the first Section of this volume.

The remaining Section is devoted to molecular theories. After a brief historical survey of the subject, the author deals first with the kinetic theory of gases, and then sketches the outlines of the

kinetic theory of liquids. Some general considerations based on

the available experimental data conclude this Section.

The work is one which will prove of very great interest to all students of molecular physics, and its value is greatly enhanced by the copious references to original memoirs.

Bulletin of the Bureau of Standards. Vol. 3, Nos. 1-4. Washington: Government Printing Office. 1907. Pp. 728.

A MERE cursory glance through these volumes is sufficient to establish the great interest and importance of the investigations now being carried out by the Washington Bureau of Standards. Here we have papers on such subjects as the calculation of mutual inductances in various cases of practical importance, a comparison of the units of luminous intensity of different countries, the establishment of the thermo-dynamic scale of temperature by means of the constant-pressure thermometer, the production of high-frequency oscillations from the electric arc, incandescent lamp photometry, the measurement of the capacity and power-factor of condensers, a determination of v, and others. No one who is anxious to keep abreast of modern progress in either pure or applied science can afford to neglect this standard publication.

### XXXIX. Intelligence and Miscellaneous Articles.

THE EVOLUTION AND DEVOLUTION OF THE ELEMENTS.
BY HUGH RAMAGE.

Messrs. A. C. and A. E. Jessup, in a very suggestive paper in the Philosophical Magazine for January, put forward as new the view that the chemical elements have evolved in groups, that is, down the vertical columns of Mendeléeff's table. view was suggested by me in a paper on "A comparative study of the spectra, densities and melting-points of some groups of elements and of the relation of properties to atomic mass," published in the Proc. Roy. Soc. vol. lxx. p. 1, 1901, and the cases of argon and tellurium were also discussed. This paper indicates the order of evolution as:-Li-Na-K-Rb-Cs and Li-Na-Cu-Ag-Au; also Be-Mg-Ca-Sr-Ba and Be-Mg-Zn-Cd-Hg, &c. The suggestion that those sub-groups beginning with copper, zinc, and gallium have been indirectly evolved from carbon, and not directly from sodium, magnesium, and aluminium respectively, receives no support from the spectra of the metals. In fact, the evidence given by the spectra, and also by certain properties of the metals, is strongly opposed to it.

The view that the formation of successive elements is attended by the escape of a large quantity of energy is contrary to that which has impressed itself upon me. The question, however, is

too complex to be dealt with in a short note.

Carrow Hill, Norwich, January 31st, 1908.

MADE.

#### THE

### LONDON, EDINBURGH, AND DUBLIN

# PHILOSOPHICAL MAGAZINE

AND

## JOURNAL OF SCIENCE.

[SIXTH SERIES.]

APRIL 1908.

The following paper was written by Lord Kelvin some months before his death, and the subject with which it is concerned was occupying his attention down to the last few days of his life, in fact, till the commencement of his last illness. Very shortly before his death he wrote out in detail a paper on "Homer Lane's Problem," which he had communicated to the Royal Society of Edinburgh in January 1907, under the title "The Problem of a Spherical Gaseous Nebula"; and it is proposed to reprint this paper, along with an appendix, written at Lord Kelvin's desire by his Private Secretary, Mr. George Green, in the next number of the Philosophical Magazine.

The present paper has been carefully corrected by Mr. Green and myself, but it was left in a perfectly finished state, and little or no editing was necessary.—J. T. BOTTOMLEY.

XL. On the Formation of Concrete Matter from Atomic Origins. By the late Lord Kelvin\*.

§ 1. COALITION, due to gravitational attraction between materials given originally in small parts widely distributed through space, is probably the most ancient history of all the bodies in the universe. What the primitive forms or magnitudes of those pieces of matter may have been can never be made known to us by historical evidence. If they had been all globes, or irregular broken solids, of diameters a few kilometres, or a few thousandths of a millimetre, and if among them all there existed all the atoms

\* Communicated by Dr. J. T. Bottomley, F.R.S.

Phil. Mag. Ser. 6. Vol. 15. No. 88. April 1908. 2 E

which at present exist, the present condition of the universe might be very much the same as it is. Towards a speculative answer we might be guided, and perhaps wrongly guided, by what we see of meteorites, stony or iron. We can hardly regard it as probable that those broken looking lumps of solid matter, with their corners and edges rounded off by melting in their final rush through our atmosphere before arriving at the Earth's surface, were primitive forms in which matter either was created, or existed through all infinity of past time. On the contrary, it may seem to us quite probable that the primitive condition of matter was atomic; perhaps every primitive particle was a separate indivisible atom; or perhaps some of the primitive particles were atoms, and some of them doublets such as the  $O_2$ ,  $N_2$ ,  $H_2$ , which we know as the molecular constituents of gaseous oxygen, gaseous nitrogen, gaseous hydrogen, according to modern chemical doctrine. Or perhaps some of the primitive particles may have been given in groups consisting of a moderate number of atoms ready for building into crystals; or they may have been given as very small complete crystals each consisting of a very large number of atoms.

§ 2. To illustrate the dynamics of the real conglomeration. which we believe to be an event of ancient history, consider an ideal case of 1083 million million million cubic metres of solid matter; the sum of their volumes being equal to the Earth's volume. Let the density of the material of each cube be equal to the Earth's mean density, 5.67. The sum of their masses will be 6.14 thousand million million million metric tons, being equal to the Earth's mass. Place them at rest in cubic order, equally distributed through a vast spherical space, of radius one thousand times the Earth's radius, and therefore of volume equal to a thousand million times the Earth's volume. Let every one of the cubes be oriented with its faces and edges parallel to the planes and lines of the cubic In this order, the lines of shortest distance between the centres of constituents are perpendicular to the three pairs of parallel faces of the cubes. The distance from centre to centre would be one metre, if the cubes were given in contact, occupying a sphere equal in bulk to the Earth. distance between the centres of nearest neighbours is therefore a kilometre, when they are given in their wide spread initial arrangement.

§ 3. Leave now the cubes all free to fall inwards in virtue of mutual gravitation. Each one of those on the bounding surface of the whole group will commence falling towards the centre of the sphere, with acceleration one millionth of the acceleration of a body falling freely near the Earth's surface: that is to say 9.8 millionths of a metre per second

per second. The centreward acceleration of all the others will be in simple proportion to their distances from the centre of the assemblage. This is easily seen by remarking that, according to Newtonian principles, the resultant force on each cube is the same as if all the cubes at less distances than its own from the centre were condensed in a point there, and all the cubes at greater distances than its own were annulled. Hence as long as the cubes all fall freely inwards their distribution remains uniform, and their boundary spherical.

§ 4. Hence the cubes, if all similarly oriented as in § 2, will, at one instant of time, all come into contact, each with all its six nearest neighbours; and for an instant they will be fitted together making a great globe of the same size as the Earth, but with angular projections at the spherical boundary according to their cubic arrangement. All the parts of this composite globe are, at the instant of first contact, moving inwards at speeds simply proportional to their distances from the centre. If the cubes were perfectly elastic, they would rebound outwards with velocities equal to those they had at the instant of first contact; and a periodic falling inwards and rebounding outwards would follow; which would continue for ever, if there were no ether to resist this gigantic oscillatory movement. But what would be done by cubes of real matter, with its true molecular constitution and imperfect elasticity, in and after such a prodigious, purely pressural, collision, is not a subject for profitable conjecture.

§ 5. Let now the cubes be placed initially at rest, with their centres arranged as in § 2, but with orientations given at random, and let them fall freely. Contacts between some neighbours will begin to occur when the shortest distances between centres are equal to  $3^{\frac{1}{2}}$ , or 1.732, metres, being the length of the body diagonal of each cube. At this instant the whole assemblage occupies  $3^{\frac{3}{2}}$ , or 5.196, times the Earth's bulk: and the average density is somewhat greater than the

density of water.

§ 6. The velocity of the outermost cubes at the instant of impact, in the case of the similar orientations of § 2, is 11,175 metres per second. If the cubes were reduced to infinitely small material points at their centres, and so could continue to fall freely to the centre of the sphere, they would all reach that point in 897 of a year from the time of our ideally assumed initial state of rest. As the material points fall towards the centre of the sphere, the mean density of the assemblage continuously increases. The following table shows the number of minutes during which the system must

continue to fall to reach the centre, after it has attained the densities indicated:—

Time before reaching the centre *.	Mean Density
47.7 minutes	0.1
21.3 ,,	0.5
15.1 ,,	1.0
6.3 ,,	5.67

If the beginning is an assemblage of cubes oriented at random, as in § 5, and with their centres in cubic order, as in § 2, contacts would commence at a time about 8 minutes earlier than the time of coming to fit exactly on the supposition of uniform orientation.

§ 7. In the case of cubes initially oriented at random, collisions will not begin simultaneously as in § 4; but will begin with a crushing to powder at colliding edges or corners. The stupendous system of collisions which follows the commencement, would, if the material of the cubes is of any known substance, metallic or rocky, cause, in the course of a few minutes, melting of the whole mass: unless the prodigious pressure in the central parts should have the effect of preventing fluidity in those parts, which does not seem probable.

§ 8. The same general description is applicable to the ideal case of a vast number of large and small fragments of any shapes, instead of our equal cubic metres of homogeneous matter; provided only that the initial distribution through the great spherical space is of uniform average density all through.

§ 9. Let us now, instead of masses large or small of concrete matter, begin with a vast number of atoms; or of atoms, and doublets such as O2, N2, H2, given at rest distributed uniformly in respect to average density through a sphere of a thousand million times the Earth's bulk: and having the sum of their masses equal to the Earth's mass. Every particle (atom or doublet) will have the same centreward velocity at the same time, as that found for the ideal cubes in § 6; until some of the atoms or doublets get into touch with neighbours, that is, come so near one another that mutual molecular forces become effective. This must be the case when the mean density is considerably less than onetenth of the density of water, as we see by considering the known properties of gases and vapours, and of liquids of small density. Hence the time during which the atoms will continue to fall freely without jostling one another must be a few minutes less than the time of getting into touch at

<sup>\*</sup> Calculated by means of a formula given on page 538 of Lord Kelvin's "Baltimore Lectures," Appendix D.

mean density somewhat greater than that of water, on the supposition of cubes randomly oriented at rest, as defined in § 5.

- § 10. When the density becomes so great that the atoms begin to seriously jostle one another, we have the first step to the formation of concrete matter from atomic origins. Our present knowledge of the properties of matter does not suffice to allow us to follow, with definite and complete understanding, the progress after this step. We can see a prodigious cloud of atoms crowding turbulently around the centre. Atoms coming from all directions meet and collide. The energy of the relative motions of the atoms is still, let us suppose, sufficient to prevent them from ever remaining in contact except during very short times when any two of them are in collision. And let us suppose the central mean density to be still considerably less than '1 of the density of water. The whole assemblage now constitutes the gaseous fluid mass which forms the subject of Homer Lane's celebrated problem\*. As long as the whole mass remains thus in gaseous condition, loss of heat to the surrounding ether allows mutual gravitation to condense the whole assemblage, doing its work by increasing the kinetic energy of the relative motions. A result, as found by the mathematical solution of Homer Lane's problem, is that all of the assemblage outside a certain distance from the centre sinks in temperature, while all within that distance rises in temperature. I may here explain that the temperature of a "perfect gas" means the kinetic energy per unit mass of all the relative translatory motions of its molecules in free paths from collision to collision.
- § 11. During the whole time of the gaseous stage which we have been considering, the crowding becomes denser and denser in the central regions, until there every atom comes to be always in collision with all its nearest neighbours. Throughout all the space around the centre in which this condition has been reached the crowd constitutes a fluid of the species called liquid. In the outlying parts the crowd is much less dense; each atom, instead of being always in collision, is in collision only during comparatively short intervals of time; and, for the rest of its time, is moving in approximately straight lines, not perceptibly disturbed by

<sup>\*</sup> J. Homer Lane, American Journal of Science, July 1870; A. Ritter, Wiedemann's Annalen, 1878...1882; Prof. A. Schuster, Brit. Assoc. Report, 1883; Sir William Thomson, Phil. Mag. vol. xxiii. p. 287, 1887; Prof. J. Perry, 'Nature,' vol. lx. 1899; T. J. J. See, Astr. Nachr. No. 4053, Bd. 169, 1905; T. J. J. See, Astr. Nachr. No. 4104, Bd. 171, 1906; Lord Kelvin, Royal Society of Edinburgh, Jan. 21, 1907; Lord Kelvin, 'Nature,' Feb. 14, 1907.

other atoms far or near. The less dense crowd of atoms in those parts constitutes a fluid of the species called gas or vapour. Every collision between two atoms in those outlying parts, and in the central region every change of speed and of direction of atomic motions, due to mutual forces between neighbouring atoms, sets ether locally in motion. The motion thus produced in ether gives rise to etherial waves which travel outwards through the outlying parts of the assemblage; and continue their outward course into void ether all around the assemblage. These etherial waves carry away gradually into infinite space the kinetic energy of the atoms, originally given to them by gravitation between all parts of the contracting assemblage. A first effect of this loss of energy would be to continue the raising of temperature in the central region, which in § 10 was said to take place during the whole of the gaseous stage of the evolution. As time advances, the dense gas or liquid in the central parts comes to a maximum of temperature. After this there is a general diminution of temperature, by the conduction and radiation of heat outwards: the whole mass goes on cooling, and is automatically kept largely stirred by irregular convection-currents, of cooled liquid flowing downwards from the surface, and of hotter and less dense liquid rising from below.

§ 12. If, as would be the case were the liquid melted iron, or water, the solidified material is less dense than the liquid at the same temperature and pressure, a continuous crust would form all over the surface of the globe; which would grow thicker and thicker inwards, by freezing of the interior liquid in contact with it, in virtue of conduction of heat outwards through the crust. This solid crust, completely enclosing a liquid, would be burst by the liquid expanding as it freezes (just as a closed water-pipe is burst by water freezing inside it). If the spherical shell bursts into many fragments these would all float. The freezing of the liquid exposed in the openings thus produced in the crust would quickly fill up the gaps; and thus the process of freezing all around would spread inwards to the centre. Such may possibly be the history of the earliest solidification of part of the Earth's mass, forming a metallic central nucleus by coalition of primeval atoms of iron, nickel, gold, platinum, or other dense metals.

§ 13. But the Earth, while not improbably metallic in its central parts, is probably in the main of "earthy" or rocky materials. It seems highly probable that, unlike the materials mentioned in § 12 which expand in freezing, all the "earthy" materials of the Earth contract in freezing. Bischoff\*, in

<sup>\*</sup> Bulletin de la Soc. Géol. 2nd series, vol. iv. p. 1312.

experiments made about eighty years ago, found that melted granite, slate, and trachyte, all contract by more than ten per cent. in freezing; and sixteen years ago, Carl Barus\* found that diabase (a partially crystalline basaltic rock) is fourteen per cent. denser than melted diabase. He found the melting temperature of diabase to be about 1170° C.; and the late Professor Roberts-Austen, by experiments which he kindly made at my request, found the melting temperatures of several different rocks under ordinary atmospheric pressure † to be as follows:—

	Melting-point.	Error.
Felspar	1520° C.	$\pm 30^{\circ}$
Hornblende about		
Mica	1440° ,,	$\pm 30^{\circ} \\ + 15^{\circ}$
Quartz		$+15^{\circ}$
Basaltabout	880° "	

§ 14. Go back now to the end of § 11, and consider the Earth after the gaseous stage of its evolution has ended in liquefaction at the centre. The temperature will sink throughout, in virtue of the automatic stirring, and of outward thermal conduction; and the amount of material in the thoroughly liquid condition will increase until the whole globe becomes liquid, except a vaporous or gaseous atmosphere of comparatively small total mass, resting on the liquid all around its spherical surface. The density of this liquid increases from surface to centre, in its earlier stages probably only because of the greater pressure; but ultimately also in consequence of subsidence of the denser chemical ingredients, after the convective currents have become too slack for thorough mixing up of all the materials.

§ 15. Crystalline freezing may begin at the surface, because of the rapid loss of heat by radiation outwards, but each solid crystal sinks because its density is greater than that of the fluid in contact with it. In sinking, it is melted and redissolved by the hotter fluid below. This process goes on until the temperature at every part of the liquid is reduced to that at which some of the ingredients such as quartz, felspar, hornblende, mica, crystallize out of the liquid, under the hydrostatic pressure at the depth of the portion considered. This formation of crystals leaves a mother liquor consisting of ingredients which freeze at a lower temperature. At this stage the portions frozen at the surface do not melt in sinking through the liquid, and they fall down to the centre, or to the central nucleus if there is one. Thus the main rigidification

\* Phil. Mag. 1893, first half-year, pp. 173-175.

<sup>†</sup> See Addendum to "The Age of the Earth as an Abode fitted for Life," Phil. Mag. 1899, first half-year, p. 89.

commences in the central region, by conglomeration into a granite of crystals descending through a vast surrounding lava ocean. The solid granite thus formed extends outwards till it comes to the surface.

§ 16. The views regarding the solidification of the Earth, described in § 15, were first published in the Proceedings of the Victoria Institute, for 1897, in an article on "The Age of the Earth as an Abode fitted for Life," republished in the Phil. Mag., Jan., 1899. From this article the following passage is quoted:—"If the shoaling of the lava ocean up "to the surface had taken place everywhere at the same time, the whole surface of the consistent solid would be the dead level of the liquid lava all round, just before its depth became zero. On this supposition there seems no possibility that our present-day continents could have risen to their present heights, and that the surface of the solid in its other parts could have sunk down to their present ocean

" depths."

§ 17. Our question is:—How can we explain why the Earth is not at present a mass of solid granite of approximately spherical surface, deviating from sphericity just so much that, if it were covered with water, the water would be at the same depth in every part, when in equilibrium under the combined influence of gravitation and centrifugal force due to its diurnal rotation? A possible, but it seems to me an almost infinitely improbable, explanation is that ocean depths are scars due to collisions with outside bodies, and mountain heights are due to matter left on the Earth by such collisions. When we look at the scarred surface of the Moon, we cannot but feel that it would be pushing possibilities beyond the verge of absurdity to attribute the geographical features of the Earth, and the corresponding features of the Moon, all to blows received by them, or matter shot down on them, from without.

§ 18. After solidification, as described in § 15, contraction by loss of heat would almost certainly produce abundance of vertical cracks, proceeding inwards from all parts of the spherical surface (on the same dynamical principle as that which explains the well-known "crackling" seen on the glaze of many kinds of pottery). But there seems no possibility that the wide-spread hollows of the Antarctic, Pacific, Atlantic, and Indian Oceans, and the great areas of elevation in the continents, Europe and Asia, Africa, America, and Australia, and the seven to ten kilometre heights in the Andes and Himalayas, can have followed, by any natural causes, merely from the condition described in § 15. I have come to this conclusion after careful consideration of the dynamics

of cooling and shrinkage, and possible cavitations, through two hundred kilometres below the surface all round the globe. It seems indeed quite certain that when the Earth came to be almost wholly solid, it must have had in itself some great heterogeneousness of constitution or figure, from which its present geographical condition had its origin. This heterogeneousness must have had its origin in some heterogeneousness of the primordial distributions of atoms: and we must abandon the uniform distribution which we chose in § 9 merely as an illustration. But we have much more than geography to account for. We have to account for:—(1) the diurnal rotation of the Earth; (2) the Earth's motion through space, at about thirty kilometres per second, relatively to the Sun; (3) the Sun's motion through space towards a point in the constellation Hercules, first indicated by Sir William Herschel, and more recently estimated at about nineteen kilometres per second, relatively to the average of sufficiently well observed stars. These three deviations from the spherical and irrotational conditions of §§ 2...16 are, it seems to me, essentially connected with the explanation of merely geographical heterogeneousness demanded in §§ 16, 17.

§ 19. Any system of bodies large or small, or of atoms, given at rest, and left subject only to mutual gravitational and collisional forces, fulfils throughout all time two laws:—

Law (1). The centre of inertia of the whole system remains

at rest.

Law (2). The sum of moments of momentum \* of the motions of all the parts, relatively to any axis through the centre of inertia, is zero.

The corresponding laws for a system set in motion in any manner, and left to move under the action of mutual forces only, are as follows:—

Law (1'). The centre of inertia of the whole system moves

uniformly in a straight line.

Law (2'). The sum of moments of momentum of the motions of all the parts, relatively to any axis through the centre of inertia, parallel to any fixed line in space, is constant.

\* (1) The momentum (a name first given in the seventeenth century when mathematicians wrote in Latin, and retained in the nineteenth and twentieth centuries) of a moving particle is the product of its mass into its velocity.

(2) The moment (a nineteenth century name) of momentum of a particle round any axis is the product of its momentum into the shortest distance of its line of motion from that axis, into the sine of the inclina-

tion of its line of motion to that axis.

(3) The moment of momentum round any axis of any number of moving particles is the name given to the sum of their moments of momentum round that axis.

It makes no difference to this definition if any set or sets of the particles

are rigidly connected to make a rigid body or rigid bodies.

Law (3). There is a certain definite line, fixed in direction, through the centre of inertia of the system, such that the sum of moments of momentum round it is greater than that round any other axis through the centre of inertia; and the moment of momentum round every axis perpendicular to it, through the centre of inertia, is zero.

That maximum moment of momentum is called the resultant moment of momentum of the system. Its axis may be called

the rotational axis of the system.

- § 20. Consider a vast assemblage of atoms, or of small bodies, given at rest at any time, distributed in any manner, uniformly or non-uniformly, through any finite volume of space. According to § 19, Law (1), the centre of inertia of the whole assemblage would remain at rest, and the total moment of momentum round every axis through it would remain zero, whatever motions the atoms receive in virtue of mutual gravitational attractions, and mutual repulsions in collision.
- § 21. Consider now separately some part of the whole assemblage, which to avoid circumlocution I shall call part S, including all the primitive atoms or particles which at present form the Solar System, but not including any other great quantity of matter. Part S has, at each instant, a definite resultant moment of momentum round a definite axis through its centre of inertia; and its centre of inertia is, at each instant, moving with a definite velocity in a definite direction. In a vast assemblage such as we were considering in § 20, which may be the whole matter of the universe (finite \* in quantity as it may with all probability be supposed to be), let there be denser parts and less dense parts. In the denser parts, there will be gravitational coalition; in the less dense parts, there will consequently be rarefaction. The present existence of the Sun is undoubtedly due to gravitational coalition in some of the denser parts. The velocity of the centre of inertia of the Solar System is due to the gravitational attractions of matter outside S, so also is the moment of momentum of the Solar System round any axis through its centre of inertia. The rarefaction of the distribution of particles, large or small, around S, leaves the matter belonging to S more and more nearly free from force acting on it from without; and it becomes more and more nearly subject to Laws (1') and (2') of § 19.

§ 22. The approximately constant momentum of the Solar System in its motion through space is chiefly the momentum of the Sun's motion, because his mass is much greater than

<sup>\*</sup> See Lord Kelvin's "Baltimore Lectures," Lec. XVI. § 15.

the sum of the masses of Jupiter and all the other planets and satellites. On the other hand, the resultant moment of momentum of the motions of all parts of the Solar System, relatively to the fixed line of greatest moment of momentum through the inertial centre of all, is chiefly due to the orbital motion of Jupiter and Saturn, and but in small part (about  $\frac{1}{60}$  of the whole) due to the Sun's axial rotation; as we see by the following table of moments of momentum, given by Mr. See \* in his paper of 1905, "Researches on the physical constitution of the heavenly bodies."

M. of m. of orbital motion, that of Sun's axial rotation

	being unity.
Sun	1.00000000
Mercury	0.00069654
Venus	0.035444
Earth	0.0517385
Mars	0.00676526
Jupiter	36.98288
Saturn	14.98374
Uranus	3.26959
Neptune	4.83260

We have not now the simple and direct gravitational coalition, by motions towards the centre of a spherical assemblage, which we had in §§ 1...16, and which gave us Homer Lane's beautiful problem of a spherical gaseous nebula. Our vast assemblage S has moment of momentum; and its main condensation has led to the formation of our rotating Sun. Local condensations of smaller portions of S, each having some share of the moment of momentum of the whole, have produced the planets, all revolving round the Sun, and rotating round their axes, in the same general direction; anti-clockwise, when viewed from the northern side of the general plane of their orbits.

§ 23. In Kant's and Laplace's Nebular Theory the local condensations, from which have been evolved the planets moving in their orbits round the Sun, and the satellites moving in their orbits round the planets, were, according to the suggestion presented to us by Saturn's rings, supposed to begin as rings of detached particles, which later became gravitationally drawn together into spheroidal groups, and formed ultimately liquid or solid approximately spherical bodies. This may probably be the true history of many of

<sup>\*</sup> Astr. Nachr. Bd. 169, Nov. 1905.

the planets and satellites; but Sir George Darwin \* has given the very important suggestion that the separation from a planet of material to become a satellite may in some cases have been a single portion of the mass, breaking away from what was earlier a rotating mass of liquid, in the shape of a figure of revolution, contracting by loss of heat, and therefore rotating with greater and greater angular velocity as it became denser.

§ 24. Suppose for example the mass which is now Earth and Moon to have been at one time a single oblate spheroid of revolution. Its figure would then have been exactly elliptic, if its rotational angular velocity, and its density, were each equal from surface to centre. If it was denser in the central regions, its figure would have been an oblate figure of revolution, but not in general exactly elliptic in its meridional sections. While the spheroid shrinks in cooling it becomes more and more oblate, till, all round the equator, gravity is exactly balanced by centrifugal force; or till the spheroid becomes lopsided, as suggested in § 25 below. Farther continued shrinkage cannot give a stable oblate figure of revolution. It might cause an equatorial belt to be detached from the main body; or the result might be as suggested in § \$ 25, 26, below.

§ 25. Poincaire's "pear-shaped" figure of equilibrium of a rotating liquid suggests the idea that the first instability produced by cooling and shrinkage, with constant moment of momentum, may possibly give rise to a stable figure with a protrusion on one side of the centre of what was the equatorial circle, and a flattening of the surface on the other side of the centre of inertia. This idea is to some degree supported by the elaborate and powerful mathematical investigations of Poincaré † and Darwin ‡ on "pear-shaped" figures of liquids rotating in stable equilibrium, under the influence

of gravity and centrifugal force.

§ 26. Continued cooling and shrinkage would produce more and more protrusion on one side of the centre of inertia,

<sup>\*</sup> Phil. Trans. 1879, p. 447, "On the Precession of a Viscous Liquid and on the remote History of the Earth"; Phil. Trans. 1880, p. 713, "On the Secular Changes in the Elements of the Orbit of a Satellite revolving about a tidally distorted Planet"; British Association Report, 1905, p. 3, Presidential Address.

<sup>†</sup> H. Poincaré, "Sur la Stabilité de l'Équilibre des Figures Pyriformes," Phil. Trans. 1902.

† Sir George Darwin, "On the Pear-shaped form of Equilibrium of a rotating Mass of Liquid," Phil. Trans. 1902; "On the Stability of the Pear-shaped figure of Equilibrium of a rotating Mass of Liquid," Phil. Trans. 1903; "On the Figure and Stability of a Liquid Satellite," Phil. Trans. 1906.

until the protrusion becomes unstable, and a comparatively small portion of the whole liquid breaks away from the main

mass, at the thin end of the "pear."

That separation must have been a sudden and violent catastrophe, however gradual may have been the changes of figure and distribution of matter which led to it. If at the time when it took place, the whole material was perfectly liquid, the act of separation would leave no permanent marks on either of the two bodies. After some moderate time of subsidence from the violent oscillations suddenly produced by the catastrophe, the Earth and Moon would have subsided into the comparatively tranquil conditions of rotating liquid spheroids, revolving round the centre of inertia of the two; disturbed from hydrostatic equilibrium only by the interior convective currents due to cooling at the surfaces; and with no prospect of ever freezing into the largely unsymmetrical shapes which we now see on the visible half of the Moon's surface, and over the whole surface of the Earth.

§ 27. To account for the evolution of present configurations and conditions, it seems to me that we must suppose the material of Moon and Earth, at the time of the separational catastrophe, to have reached some such condition as that described in § 15:—a conglomeration of crystals with still liquid lava filling all the interstices between them. Such a conglomeration would have plasticity enough to pass through the changes of figure which, according to Darwin's theory, the material of Moon and Earth must have experienced before the separational catastrophe: and yet may have possessed sufficient subpermanent or permanent resistance against change of shape to allow them to keep permanent traces of the wounds

left on the two bodies by the convulsive separation.

§ 28. The scar, and subsequent surgings, left on the semi-plastic Earth by the tearing away of the Moon from it might account for persisting deviation from rotational symmetry, and from equilibrium of gravity and centrifugal force, as great as that which is presented by the elevations of Africa, Asia, Europe, America, and the depths of the Atlantic, Pacific, and Indian Oceans. If, at the time when the Moon left the Earth, the material was all in the semi-solid semi-plastic condition of granite conglomerate, with a mother liquor of melted basalt in the interstices among the crystals, this quasi unset Portland cement, constituting the two bodies, might well in the course of fifty or one hundred million years become as nearly solid as we know both the Earth and Moon to be at present. It must however be quite understood that the present features of the Earth, with mountains and ravines,

and ocean depths, have been produced by long continued

geological actions of upheavals and erosion.

§ 29. Immediately after the separation, the Moon, about at of the Earth's mass, would begin moving from the perigee of a somewhat approximately elliptic orbit round the centre of inertia of Earth and Moon, much disturbed on account of the great and violently changing deviations from sphericity of the two masses. The period of this orbital motion of the two bodies round their centre of inertia would be longer than the rotational period of the Earth, which would be but little changed by the catastrophe. In becoming rounded into a spheroidal form, the Moon would come to rotate round its own axis in a somewhat shorter period than that of the whole mass before the separation. Thus, in the beginning of the new regime, we have three different periods; the shortest being the rotational period of the Moon round an axis through her centre of inertia; somewhat longer than this the rotational period of the Earth; and considerably longer than it, the orbital period of the two bodies round their centre of inertia.

§ 30. The changes of shape of the two semiplastic spheroids in their subsequent motions under the influence of mutual gravitation between all their parts, would give rise to a loss of energy: while the total moment of momentum would remain unchanged. The main action would be loss of kinetic energy of the Earth and Moon, by transformation into heat of quasi-tidal work within the two bodies. Essentially concomitant features would be augmentation of the distance between them, involving work done against mutual gravity, and gradual transformation of the moment of momentum of their rotations into augmentation of the moment of momentum of their orbital motions round the centre of inertia of the two. The energy of the initial rotation of the Moon would be small compared with that of the Earth. The whole kinetic energy of the rotations, and the motions of centres of inertia, of the two bodies, at the present time exceeds by a relatively small quantity the present kinetic energy of the Earth's rotation. The work done in separating the Moon to its present distance from the Earth, and in giving it the kinetic energy of its orbital motion, has been wholly drawn from the Earth's rotational kinetic energy at the time of the disruption, with the exception of a small contribution derived from the Moon's initial kinetic energy of rotation. A comparatively early result of the motions of the two bodies must have been to bring the Moon to keep always the same face to the Earth as she does at the present time.

§ 31. Sir George Darwin, with comprehensively penetrating dynamical insight, has traced the course of events following the stage reached in § 29. He has given a reasonable account of the evolution of the present eccentricity of the Moon's orbit; and he has made the remarkable and important discovery that the axis of the Earth's rotation could not remain as it is at the stage of § 29, perpendicular to the plane of the orbital motion of Earth and Moon. We might readily enough work out the general character of the motions and transformations that would follow the stage of § 29, if the Earth's and Moon's rotational axes did in reality remain perpendicular to the plane of their orbital motions. But Darwin finds that this possible and easily understood association of motions would be unstable; and that the slightest deviation from exact perpendicularity of the Earth's axis to the orbital plane would become, not diminished but, augmented by the Earth's viscous resistance against change of shape. With this hint it is almost as easy for us to see, by dynamical reasoning, that the Earth's axis must, through millions of years, have become more and more oblique to the orbital plane, as it is, for us, with Archibald Smith's hint\*, to see that a "teetotum" or a boy's spinningtop, having a well rounded bearing point, and set to spin at a sufficiently high speed round an axis oblique to the vertical. and dropped on a hard horizontal plane, will in a short time, perhaps less than a minute, be found spinning round a fixed exactly vertical axis ("sleeping"), and will go on so for ever, if the materials of the top and plane are perfectly hard. and if there is no resistance of the air.

§ 32. Darwin's theory of the birth of the Moon might seem improbable; might seem even an extravagant attempt in evolutionary philosophy, insufficiently founded on knowledge. In reality it is rendered highly probable, it is indeed forced upon us, by tracing backwards to earlier and earlier times the dynamical antecedents of the present conditions of Earth,

Moon, and Sun.

§ 33. A hundred years before the doctrine of energy thoroughly entered the minds of mathematicians and naturalists, Kant made known the truth that the Earth's rotational velocity is diminished by tidal friction. When we consider the dynamics on which this statement is founded, we see that it implies reactive forces gravitationally exerted on the Sun and Moon by terrestrial waters. Ignoring the Sun, as less influential than the Moon in respect to the tides, we

<sup>\* &</sup>quot;Note on the Theory of the Spinning Top," Camb. Math. Journal, 1839, vol. i. p. 42.

"see that the mutual action between the Moon and the Earth "must tend, in virtue of the tides, to diminish the rapidity "of the Earth's rotation, and increase the moment of the "Moon's motion round the Earth." \* . . . . "The tidal defor-"mation of the water exercises the same influence on the "Moon as if she were attracted not precisely in the line "towards the Earth's centre, but in a line slanting very "slightly, relatively to her motion, in the direction forwards." "The Moon, then, continually experiences a force forward in "her orbit by reaction from the waters of the sea. Now, it "might be supposed for a moment that a force acting "forwards would quicken the Moon's motion; but, on the "contrary, the action of that force is to retard her motion. "It is a curious fact easily explained, that a force continually "acting forward with the Moon's motion will tend, in the "long run, to make the Moon's motion slower, and increase "her distance from the Earth."\*

§ 34. Thus we see that in the present regime the Moon is getting farther and farther from the Earth, and the Earth's rotational velocity is becoming less and less; the sum of moments of momentum being thus kept constant. Hence in more and more ancient times, the Moon must have been nearer and nearer to the Earth, and the Earth's rotational velocity must have been greater and greater. Trace then the course of motions backwards for a sufficient number of millions of years, and we find the Earth much hotter than at present, and in the semi-solid semi-plastic condition described in § 28 above. The distance of the Moon from the Earth must then as now have been increasing, and the Earth's rotational velocity then as now diminishing. But these two changes must have been much more rapid then than now, because of the viscosity of the semi-solid material of the Earth, and because of the Moon's shorter distance from the Earth and therefore greater gravitational influence on the Earth, then than now. Sir George Darwin had perfect right to trace the regime backwards, until there was contact and continuity between the Earth and Moon. The continuity of the whole mass must have come to an end with the sudden and violent catastrophe described in § 28 above, to which Sir George Darwin boldly went back with sober truthfulness. It is conceivable that meteorites large or small may have at various times produced disturbances; but I cannot see any probability for any

<sup>\*</sup> Quoted from Sections 7 and 14 respectively of an address by Sir William Thomson, to the Geological Society of Glasgow, "On Geological Time," Feb. 27, 1868; republished in Lord Kelvin's 'Popular Lectures and Addresses,' vol. ii., see pp. 21 and 33.

other history of Earth and Moon, differing materially from

that which Darwin has given us.

§ 35. Returning now to § 1, an unanswerable question occurs:—Were the primordial atoms relatively at rest in the most ancient time, or were they moving with velocities, relative to fixed axes through the centre of inertia of the whole, sufficiently great to give any considerable contribution to the present kinetic energy of the universe? It is conceivable that all the atoms were relatively at rest in the most ancient time, and that "the potential energy of gravitation may be in reality the ultimate created antecedent of all the motion, heat, and light at present in the universe"\*.

- XLI. On the Theory of Surface Forces.—III. The Physical Meaning of the Unstable Part of the Isotherm of James Thomson. By G. BAKKER †.
- § 1. The Equations of Lord Kelvin for the Pressure of the Vapour in the neighbourhood of a Curved Capillary Layer.

In this periodical  $\ddagger$  I have demonstrated, that in a plane capillary layer of a liquid, which is in contact only with its vapour, the hydrostatic pressure  $(p_1)$  perpendicular to its surface is equal to the vapour-pressure, but that on the contrary the hydrostatic pressure  $(p_2)$  parallel to the surface of the capillary layer has a gradient in the direction of the normal to the surface. The relation between the pressure  $p_2$ 

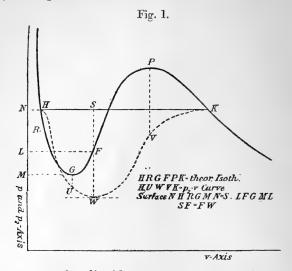
and  $\frac{1}{\rho}$ , where  $\rho$  denotes the density in a point of the capillary layer, was given by the curve HUWVK of fig. 1 (p. 414); the curve HRGFPK presents the theoretical isotherm of James Thomson. I will now extend these considerations to a capillary layer which has the form of a spherical shell. Therefore I consider firstly a spherical bulb of vapour in equilibrium in the interior of a liquid. The capillary layer round about the vapour is in this case a spherical shell, and

<sup>\*</sup> Quoted from "On Mechanical Antecedents of Motion, Heat, and Light," Brit. Assoc. Rep., Part II., 1854; Edin. New Phil. Journal, vol. i., 1855; Comptes Rendus, vol. xl., 1855; republished in Sir William Thomson's 'Math. and Phys. Papers,' vol. ii. p. 34.

<sup>†</sup> Communicated by the Author. † "On the Theory of Surface Forces—II.": Phil. Mag. Oct. 1907, pp. 515 & 526.

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the surface of the capillary layer is therefore concave to the side of the vapour. Because the forces of attraction between



the elements of a liquid or vapour are perceivable through only a very small range, the potential V of these forces at some internal point depends only on the elements embraced in the sphere of action of which it is the centre, and should be thus for a homogeneous phase proportionate to the density  $\rho$ . For the potential function of the forces of attraction we have thus:

$$\phi(r) = -f \frac{e^{-qr}}{r},$$

which gives for the potential V the following differential equation:

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = q^2 V + 4\pi f \rho. \qquad (1)$$

For our case, and in many others, it is necessary to introduce instead of the coordinates x, y, z more general coordinates and to transform the left of the equation (1) into a more general expression. For this purpose, we divide the whole space into elements of volume by a set of orthogonal surfaces. Such a system of surfaces cut one another, as every one knows, according to the theorem of Dupin, into lines of curvature. The differentials of these curves we shall

\* "On the Theory of Surface Forces-I.": Phil. Mag. Dec. 1906, p. 558.

denote by du, dv, and dn. For the potential energy of the agent, which presents mathematically the fluid, we have found:

$$W = -\frac{1}{8\pi f} \iiint R^2 dx \, dy \, dz - \frac{q^2}{8\pi f} \iiint V^2 dx \, dy \, dz^*, \quad (2)$$

where R denotes the force acting on unit of mass.

This equation can be written:

$$W = -\frac{1}{8\pi f} \iiint \left\{ \left( \frac{\partial V}{\partial u} \right)^2 + \left( \frac{\partial V}{\partial v} \right)^2 + \left( \frac{\partial V}{\partial n} \right)^2 \right\} du \, dv \, dn$$
$$-\frac{g^2}{8\pi f} \iiint V^2 du \, dv \, dn.$$

The variation of W gives:

$$\delta \mathbf{W} = -\frac{1}{4\pi f} \iiint \left\{ \frac{\partial \mathbf{V}}{\partial u} \delta \frac{\partial \mathbf{V}}{\partial u} + \frac{\partial \mathbf{V}}{\partial v} \delta \frac{\partial \mathbf{V}}{\partial v} + \frac{\partial \mathbf{V}}{\partial n} \delta \frac{\partial \mathbf{V}}{\partial n} \right\} du \, dv \, dn$$
$$-\frac{q^2}{4\pi f} \iiint \mathbf{V} \delta \mathbf{V} \, du \, dv \, dn. \qquad (3)$$

We put:  $du dv = dS_1$ ,  $du dn = dS_2$ ,  $dv dn = dS_3$ ; hence:

$$\iiint \frac{\partial \mathbf{v}}{\partial u} \delta \frac{\partial \mathbf{v}}{\partial u} d\mathbf{S}_3 du = \iiint \frac{\partial \mathbf{v}}{\partial u} \frac{\partial \mathbf{v}}{\partial u} du d\mathbf{S}_3 = \iiint \frac{\partial \mathbf{v}}{\partial u} d\mathbf{S}_3 \delta \mathbf{v}$$
$$-\iiint \delta \mathbf{v} \frac{\partial \left(\frac{\partial \mathbf{v}}{\partial u} d\mathbf{S}_3\right)}{\partial u} du.$$

The integral refers to the whole space, and the surface-integral, being therefore null, contributes nothing to the value of  $\delta W$ .

By the development of all the terms of the first volume-integral of (3) we get:

$$\delta \mathbf{W} = \frac{1}{4\pi f} \iiint \delta \mathbf{V} \left\{ \frac{\partial \left(\frac{\partial \mathbf{V}}{\partial u} d\mathbf{S}_{2}\right)}{\partial u} du + \frac{\partial \left(\frac{\partial \mathbf{V}}{\partial v} d\mathbf{S}_{3}\right)}{\partial v} dv + \frac{\partial \left(\frac{\partial \mathbf{V}}{\partial n} d\mathbf{S}_{1}\right)}{dn} \right\} - \frac{q^{2}}{4\pi f} \iiint \mathbf{V} \delta \mathbf{V} du dv dn. \qquad (4)$$

We will now consider the "parallelepiped curvilinear" constructed upon the differentials du, dv, and dn, which meet

\* "On the Theory of Surface Forces—I.": Phil. Mag. Dec. 1906, p. 559.

in the same point. The base of this parallelepiped is:  $dS_1 = du \, dv$ . If we denote the element of the surface opposite to  $dS_1$  by  $dS_1'$  we have, neglecting the infinitely small of higher order,

$$\frac{\partial}{\partial n} (dS_1) = \frac{dS_1' - dS_1}{\partial n}.$$

We find therefore

$$\frac{\partial \left(\frac{\partial V}{\partial n}dS_1\right)}{\partial n}dn = \frac{\partial \frac{\partial V}{\partial n}}{\partial n}dS_1dn + \frac{\partial V}{\partial n}(dS_1' - dS). \quad . \quad (5)$$

du and dv are the elements of the curves of curvature in the considered point of the surface  $S_1$ . Therefore

$$dS_{1}' = du \, dv \left( 1 + \frac{dn}{R_{1}} \right) \left( 1 + \frac{dn}{R_{2}} \right) = dS_{1} + \left( \frac{1}{R_{1}} + \frac{1}{R_{2}} \right) du \, dv \, dn.$$
 (6)

If the surface-elements, denoted by  $dS_1$ , be specially the elements of the equipotential surfaces and if dn denotes the differentials of the lines of force, we have

$$\frac{\partial u}{\partial \frac{\partial u}{\partial V}} = 0, \quad \frac{\partial v}{\partial \frac{\partial v}{\partial V}} = 0, \quad \frac{\partial u}{\partial V} = 0, \quad \frac{\partial u}{\partial V} = 0,$$

and the equation (4) gives with the aid of (5) and (6):

$$\delta \mathbf{W} = \frac{1}{4\pi f} \int \delta \mathbf{V} \left\{ \frac{\partial \frac{\partial \mathbf{V}}{\partial n}}{\partial n} + \frac{\partial \mathbf{V}}{\partial n} \left( \frac{1}{\mathbf{R}_1} + \frac{1}{\mathbf{R}_2} \right) - q^2 \mathbf{V} \right\} d\tau . \quad (7)$$

where  $d\tau$  denotes the element of volume.

For the potential energy of the forces of attraction we have also the general expression:

$$W = \frac{1}{2} \int V \rho d\tau.$$

Varying only the density, we have

$$\int \nabla \delta \rho \, d\tau = \int \rho \partial \nabla d\tau,$$

and thus

The equalization of (7) and (8) gives:

$$\frac{\partial \frac{\partial \mathbf{V}}{\partial n}}{\partial n} + \left(\frac{1}{\mathbf{R}_1} + \frac{1}{\mathbf{R}_2}\right) \frac{\partial \mathbf{V}}{\partial n} = q^2 \mathbf{V} + 4\pi f \rho. \quad . \quad (9)$$

For a homogeneous agent we have:

$$\frac{\partial \overline{\partial n}}{\partial \overline{\partial n}} = 0$$
, and  $\frac{\partial V}{\partial n} = 0$ .

The differential equation passes therefore for a homogeneous agent into the equation:

$$\nabla + 4\pi f \lambda^2 \rho = 0$$
.

According to the theory of Gauss and van der Waals the potential energy of the forces of attraction must be in this case

$$V = -2a\rho$$

where a denotes the coefficient of the expression for the so-called molecular pressure of Laplace. Hence

$$2\pi f \lambda^2 = a$$
.

For a capillary layer, having the form of a spherical shell, concave towards the vapour, we have therefore:

$$\lambda^2 \frac{d^2 \mathbf{V}}{dh^2} - \frac{2\lambda^2}{\mathbf{R}} \frac{d\mathbf{V}}{dh} = \mathbf{V} + 2a\rho, \qquad . \qquad . \qquad (10)$$

where R denotes the radius of the sphere of equal density, which passes through the considered point, while dh indicates the differential of the normal (radius) to the surface of the capillary layer. This differential is reckoned positive in the direction: liquid —> vapour.

If p denotes the pressure for a point of the theoretical isotherm, which corresponds to the density of the considered point in the capillary layer\* we call  $\mu = \int v dp$  the thermodynamical potential in the considered point of the capillary layer. If  $\mu_1$  indicates the value of  $\mu$  in the homogeneous phase of the liquid we have:

$$V + 2a\rho = \mu_1 - \mu \uparrow$$
. . . . . (11)

For the homogeneous liquid- and vapour-phases, which limit the capillary layer, the potential V may be expressed by the formula of Gauss and van der Waals:

$$V = -2a\rho$$

and therefore

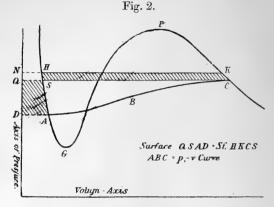
#### $\mu_l = \mu_{\bullet}$

when  $\mu_l$  and  $\mu_v$  indicate resp. the value of the thermodynamical potential in the liquid and in the vapour. In

\* We say that a point of the theoretical isotherm corresponds with a point in the capillary layer, when the specific volume of the first has the reciprocal value of the density of the latter.

† Phil. Mag. October 1907, p. 516, equation (4).

fig. 2 HGPK presents the theoretical isotherm, and surface NHADN gives the absolute value of the integral  $\mu = \int v dp$ .



If the points A and C correspond with the points of the spherical surfaces, which limit the capillary layer, the equality of the thermodynamical potentials requires therefore:

### Surface NHADN=Surface NKCQN.

We put:  $NH = v_1$ ,  $KN = v_2$ ,  $DA = v_1'$  and  $QC = v_2'$ , and we consider approximately NHAD as a trapezium. We have then:

$$(v_1+v_1')(p_1-p_l)=(v_2+v_2')(p_1-p_v).$$
 (12)

In this equation  $v_1$  and  $v_2$  indicate respectively the specific volume of the liquid and vapour in contact with a plane capillary layer;  $v_1$  and  $v_2$  on the contrary denote respectively the specific volume of the liquid and vapour in contact with a capillary layer, which limits a spherical bubble of vapour. In the same manner  $p_1$  indicates the pressure of the vapour in contact with a plane capillary layer, while  $p_l$  and  $p_v$  are respectively the pressures in the liquid and in the vapour, when these homogeneous phases are separated by a capillary layer, which has the form of a spherical shell.

From the equations (10) and (11) we may deduce:

$$\lambda^2 \frac{d^2 V}{dh^2} - \frac{2\lambda^2 dV}{R} = \mu_1 - \mu, \qquad (10 a)$$

where  $\mu_1 = \mu_l$  indicates the value of the thermodynamical potential in the liquid.

By differentiating (10 a), we obtain:

$$\lambda^2 d \frac{d^2 \mathbf{V}}{dh^2} - \frac{2\lambda^2}{\mathbf{R}} d \frac{d \mathbf{V}}{dh} = -v dp,$$

and on substituting the value of  $\rho$  in (10) we find by integrating,

 $p_v - p_l = \frac{\lambda^2}{a} \int_1^2 \frac{1}{R} \left(\frac{dV}{dh}\right)^2 dh.$ 

If R denotes a value between the minimum and maximum values of the radii of the spheres, which limit the capillary layer, we may write:

 $p_v - p_l = \frac{2}{R} \cdot \frac{\lambda^2}{2a} \int_1^2 \left(\frac{dV}{dh}\right)^2 dh. \qquad (13)$ 

Now we have for the cohesion respectively in the direction of the lines of force and perpendicular to this direction\*:

$$S_1 = -\frac{1}{8\pi f} \left\{ \left( \frac{dV}{dh} \right)^2 - \frac{V^2}{\lambda^2} \right\}$$
and
$$S_2 = \frac{1}{8\pi f} \left\{ \left( \frac{dV}{dh} \right)^2 + \frac{V^2}{\lambda^2} \right\}.$$

When further  $p_1$  and  $p_2$  denote respectively the hydrostatic pressures in the same directions we have also  $\dagger$ :

$$S_2 - S_1 = p_1 - p_2$$

Hence:

and

$$p_1 - p_2' = \frac{1}{4\pi f} \left(\frac{dV}{dh}\right)^2$$
.

The total departure from the law of Pascal being the surface-tension H of Laplace, we have thus:

$$\mathbf{H} = \frac{1}{4\pi f} \int_{1}^{2} \left(\frac{d\mathbf{V}}{dh}\right)^{2} dh = \frac{\lambda^{2}}{2a} \int_{1}^{2} \left(\frac{d\mathbf{V}}{dh}\right)^{2} dh,$$

and equation (13) becomes

$$p_v - p_l = \frac{2H}{R} \dots \dots (13a)$$

By the aid of (12) we can write therefore the equations of Lord Kelvin in the form:

$$p_{v} = p_{1} - \frac{v_{1} + v_{1}'}{v_{2} + v_{2}' - (v_{1} + v_{1}')} \cdot \frac{2H}{R}$$

$$p_{l} = p_{1} - \frac{v_{2} + v_{2}'}{v_{2} + v_{2}' - (v_{1} + v_{1}')} \cdot \frac{2H}{R}$$

$$, \qquad (14)$$

\* Phil. Mag. Dec. 1906, p. 564.

† Phil. Mag. Dec. 1906, p. 564. The hydrostatic pressure  $p_1$  is therefore in the direction of the radius of the capillary layer.

§ 2. The curves, which present the relations between the hydrostatic pressure  $p_1$  in the direction of the normal to the surface of the capillary layer and the reciprocal value  $v = \frac{1}{0}$  of the density in the considered point.

If  $\theta$  denotes the thermic pressure \* in a point of the capillary layer, we may consider the hydrostatic pressure in every direction as the difference between  $\theta$  and the cohesion. In the direction normal to the surface of the capillary layer, we have therefore:

and (see above) 
$$p_1 = \theta - S_1$$
 
$$S_1 = \frac{V^2}{4a} - \frac{\lambda^2}{4a} \left(\frac{dV}{dh}\right)^2.$$

Hence

$$p_1 = \theta - \frac{V^2}{4a} + \frac{\lambda^2}{4a} \left(\frac{dV}{dh}\right)^3.$$

Differentiating in the direction of the normal h, we find thus:

$$\frac{dp_1}{dh} = \frac{d\theta}{dh} - \frac{\mathbf{V}}{2a} \frac{d\mathbf{V}}{dh} + \frac{\mathbf{\lambda}^2}{2a} \frac{d\mathbf{V}}{dh} \frac{d^2\mathbf{V}}{dh^2}.$$

Further:

$$d\theta = -\rho dV$$

and

$$\lambda^2 \frac{d^2 V}{dh^2} - V - 2a\rho = \frac{2\lambda^2 dV}{R dh}$$
 {see above, equation (10)}.

Hence

$$\frac{dp_1}{dh} = \frac{\lambda^2}{a} \left(\frac{d\mathbf{V}}{dh}\right)^2 \cdot \frac{1}{\mathbf{R}} = \frac{1}{4\pi f} \left(\frac{d\mathbf{V}}{dh}\right)^2 \cdot \frac{2}{\mathbf{R}}.$$
 (15)

Now we have found above for the departure from the law of Pascal .

$$p_1 - \hat{p}_2 = \frac{1}{4\pi f} \left(\frac{d\mathbf{V}}{dh}\right)^2.$$

Equation (15) gives therefore:

$$\frac{dp_1}{dh} = \frac{2(p_1 - p_2)}{R}. \quad . \quad . \quad . \quad (16)$$

We have thus the following theorem:

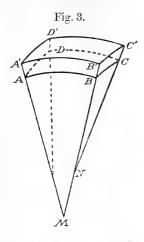
The gradient of the hydrostatic pressure  $p_1$  in the direction of the normal to the surface in a point of a capillary layer, which has the form of a spherical shell, is the product of the departure from the law of Pascal and the curvature.

\* The thermic pressure is the power of repulsion in the theory of Young.

This theorem may also be demonstrated without the aid of

a special potential function in the following manner:

We divide the capillary layer (that may be limited by a arbitrary surface) into volume-elements by a system of orthogonal surfaces, of which one is presented by a surface of equal density. Every element, such as ABCD A'B'C'D'



must be in equilibrium under the action of the hydrostatic pressures round about this element\*. Let  $R_1$  and  $R_2$  denote respectively the radii of curvature of the elements AB and BC of the lines of curvature on a surface of equal density, while  $\alpha$  and  $\beta$  be the angles AMB and BNC. Further, we indicate the hydrostatic pressures respectively in a direction perpendicular to the surfaces of equal densities and parallel to these surfaces by  $p_1$  and  $p_2$ , while the differential AA' of the normal MA is denoted by dh. The pressures on the faces BCC'B' and ADD'A' are thus  $p_2 \times$  surface BCC'B' =  $p_2\beta R_2dh$  and the pressures on the faces ABB'A' and DCC'D':  $p_2\alpha R_1dh$ . The components of these hydrostatic pressures in the direction of the normal through the middle of ABCD are thus:

$$p_2\beta R_2dh \sin \frac{1}{2}\alpha$$
 and  $p_2\alpha R_1dh \sin \frac{1}{2}\beta$ .

For the pressures on the elements of surface ABCD and A'B'C'D', we have

$$p_1 \alpha \mathbf{R}_1 \cdot \beta \mathbf{R}_2$$
 and  $\left(p_1 + \frac{dp_1}{dh} dh\right) \alpha (\mathbf{R}_1 + dh) \cdot \beta (\mathbf{R}_2 + dh)$ .

<sup>\*</sup> Gravitation is not considered.

When we substitute  $\frac{1}{2}\alpha$  for  $\sin \frac{1}{2}\alpha$  and  $\frac{1}{2}\beta$  for  $\sin \frac{1}{2}\beta$ , the equation of equilibrium may be written:

$$\boldsymbol{\alpha}\boldsymbol{\beta} \mathbf{R}_2 p_2 dh + \boldsymbol{\alpha}\boldsymbol{\beta} \mathbf{R}_1 p_2 dh = \left(p_1 + \frac{dp_1}{dh} dh\right) \boldsymbol{\alpha} (\mathbf{R}_1 + dh) \boldsymbol{\beta} (\mathbf{R}_2 + dh) - p_1 \boldsymbol{\alpha} \boldsymbol{\beta} \mathbf{R}_1 \mathbf{R}_2.$$

Neglecting the infinitely small of higher order and omitting the common factors dh,  $\alpha$  and  $\beta$ , we find:

$$p_{2}R_{2}+p_{2}R_{1}=p_{1}R_{1}+p_{1}R_{2}-\frac{dp_{1}}{dh}R_{1}R_{2}...$$
or
$$-\frac{dp_{1}}{dh}=(p_{1}-p_{2})\left(\frac{1}{R_{1}}+\frac{1}{R_{2}}\right). \qquad (16 a)$$

For a capillary layer which has the form of a spherical shell, we have thus:

$$\frac{dp_1}{dh} = -\frac{2(p_1 - p_2)}{R}, \quad . \quad . \quad . \quad (17)$$

If we consider the positive in the direction: liquid-vapour, equation (17) corresponds to a spherical drop of liquid, surrounded by vapour; for, in fig. 3, we have considered dh positive in a direction *opposite* to the direction of the radius of curvature. The equation (16 a) may be expressed as the following general theorem:

The gradient of the hydrostatic pressure  $p_1$  in a direction normal to the surfaces of equal density in a point of an arbitrary capillary layer is equal to the product of the departure from the law of Pascal and the curvature of the surface of equal density, that passes through the considered point.

If the curvature is null and the capillary layer therefore plane, we have properly:

$$\frac{dp_1}{dh} = -\frac{2(p_1 - p_2)}{\infty} = 0,$$

or  $p_1 = \text{constant} = \text{pressure of the vapour.}$ 

For a capillary layer, which limits a spherical bubble of vapour, we have already found:

$$\frac{dp_1}{dh} = \frac{2(p_1 - p_2)}{R}. . . (16)$$

Integrating the equation (16), we find immediately the theorem of Lord Kelvin:

$$p_v - p_l = \frac{2}{R} \int_1^2 (p_1 - p_2) dh = \frac{2H}{R}.$$

Now we have (see above) for every point of the capillary layer:

$$p_1 - p_2 = \frac{1}{4\pi f} \left(\frac{dV}{dh}\right)^2$$

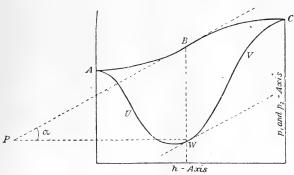
Hence

$$p_1 > p_2$$
, and thus always  $\frac{dp_1}{dh} > 0$ .

For a capillary layer, which limits a bubble of vapour, the hydrostatic pressure  $p_1$  increases therefore continually in the direction: liquid-vapour. The value  $p_l$  of  $p_1$  in the homogeneous phase of the liquid is presented in fig. (4) by the ordinate of the point A, and the value  $p_v$  in the homogeneous phase of the vapour by the ordinate of the point C. If PB is the tangent at a point B of the curve ABC, we have

PW = BW cot 
$$\alpha = (p_1 - p_2) : \frac{dp_1}{dh} = \frac{1}{2}R.$$

Fig 4.



In the same manner, as I have demonstrated for a plane capillary layer \*, we may prove that the curve, which represents the potential V of the attractive forces between the volume-elements as a function of h, has only one point of inflexion, or that  $\frac{dV}{dh}$  has only one maximum value. Because  $\frac{dp_1}{dh}$  is proportionate to  $\frac{1}{R} \left(\frac{dV}{dh}\right)^2$  {see equation (15)}, the curve,

which presents  $p_1$  as a function of h, must therefore have likewise a point of inflexion and the  $p_1-h$ -curve has thus a form as the curve ABC in fig. 4. The equation (15) may be written:

$$\frac{dp_1}{dv} = \frac{1}{4\pi f} \left(\frac{d\mathbf{V}}{dh}\right)^2 \cdot \frac{2}{\mathbf{R}} \frac{dh}{dv}.$$

\* Phil. Mag. Oct. 1907, p. 517.

If therefore the gradient  $\frac{dv}{dh}$  of the reciprocal value of the density  $\rho\left(v=\frac{1}{2}\right)$  has the same sign for every point of the capillary layer\*, the curve, which presents  $p_1$  as a function of v, has a form as the curve ABC in fig. 2, where HGPK presents the theoretical isotherm.

 $\S$  3. The curves, which represent the relations between the hydrostatic pressure p2 in a direction normal to the radius and the reciprocal value  $v = \frac{1}{\rho}$  of the density in the considered point of the capillary layer.

The radius of the capillary layer, which has the form of a spherical shell, gives the direction of the lines of force. The hydrostatic pressure  $p_2$  is therefore in a direction *normal* to the lines of force. If  $\theta$  denotes the thermic pressure and S<sub>2</sub> the cohesion in the designed direction, we have

$$p_2 = \theta - S_2$$
.

Now the cohesion  $S_2$  in a direction normal to the lines of force is given by the formula:

$$S_2 = \frac{1}{8\pi f} \left\{ \left( \frac{dV}{dh} \right)^2 + \frac{V^2}{\lambda^2} \right\}^{\dagger}.$$

Hence

$$p_2 = \theta - \frac{\mathbf{V}^2}{8\pi f \lambda^2} - \frac{1}{8\pi f} \Big(\frac{d\mathbf{V}}{dh}\Big)^2.$$

In the direction of the lines of force the cohesion S<sub>1</sub> is given by

$$S_1 = -\frac{1}{8\pi t} \left\{ \left( \frac{dV}{dh} \right)^2 - \frac{V^2}{\lambda^2} \right\}.$$

Therefore:

$$p_1 = \theta - \frac{V^2}{8\pi f \lambda^2} + \frac{1}{8\pi f} \left(\frac{dV}{dh}\right)^2.$$

 $a=2\pi f\lambda^2$ . (See above p. 417.) Further we have:  $_{
m Hence}$ 

$$\frac{p_1 + p_2}{2} = \theta - \frac{V^2}{4a}$$
. (18)‡

\* In the Ann. der Phys. xvii. p. 478 (1905) I have demonstrated the great probability of this supposition.

† Phil. Mag. Dec. 1906, p. 560. ‡ The hydrostatic pressures  $p_1$  and  $p_2$  may be also considered respectively as the maximum and minimum value of the pressures in the considered point.

We will denote half the sum of the max, and min. value of the hydrostatic pressure by p, and write:

$$\mathfrak{p} = \theta - \frac{\mathbf{V}^2}{4a}. \qquad (18 a)$$

In differentiating (18 a) we have:

$$\frac{d\mathfrak{p}}{dv} = \frac{d\theta}{dv} - \frac{2V}{4a} \frac{dV}{dv} = \frac{d\theta}{dv} \Big( 1 + \frac{Vv}{2a} \Big),$$

because

$$d\theta = -\rho dV$$
.

Further we have:

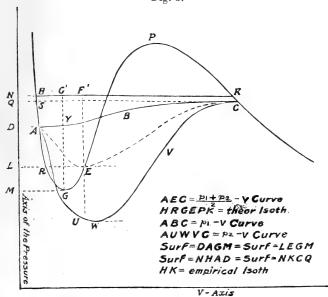
$$V + 2a\rho = \mu_1 - \mu^*.$$

$$\frac{d\mathfrak{p}}{dv} = \frac{d\theta}{dv} \frac{\mu_1 - \mu}{2a\rho}.$$

Thus

 $\mu$  is the thermodynamic potential of the homogeneous phase, which corresponds with the density of the considered point in the capillary layer. When the index 1 corresponds to the homogeneous phase of the liquid, we have

$$\mu - \mu_1 = \int_1 v dp.$$
 Fig. 5.



\*If we construct, therefore, in fig. 5 the curve AEC, which presents half the sum of the pressures  $p_1$  and  $p_2$  ( $\mathfrak{p}$ ) as a \* Phil. Mag. October 1907, p. 516, equation (4). See also above.

function of  $v = \frac{1}{\rho}$ , so is the point E of the curve, where the ordinate has its maximum value, exactly the point of the theoretical isotherm for which  $\mu = \mu_1$ , or:

When, namely,  $\mu = \mu_1$ , the equation

$$V + 2a\rho = \mu_1 - \mu$$

gives

$$V = -2a\rho$$

and the equation (18 a) becomes

$$\mathfrak{p} = \theta - \alpha \rho^2.$$

Now, we have for the theoretical isotherm:

$$p = \theta - a\rho^2$$
.

Hence

$$\mathfrak{p}=p$$
.

# § 4. The capillary layer, which envelops a spherical drop of liquid.

Hitherto we have considered a bubble of vapour, which was enveloped by liquid. Let us now consider a spherical drop of liquid enveloped by the vapour. The capillary layer, which envelops the liquid, is in this case convex on the side of the vapour, and the differential equation for the potential of the forces of cohesion is, instead of the equation (10 a) above:

$$\lambda^2 \frac{d^2 \mathbf{V}}{dh^2} + \frac{2\lambda^2}{\mathbf{R}} \frac{d\mathbf{V}}{dh} = \boldsymbol{\mu}_{\scriptscriptstyle 1} - \boldsymbol{\mu},$$

while the difference between  $p_v$  and  $p_l$  is found by the aid of the equation (13) in changing R into -R. Hence

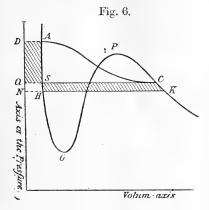
$$p_l - p_v = \frac{2}{R} \frac{\lambda^2}{2a} \int_1^2 \left(\frac{d\mathbf{V}}{dh}\right)^2 dh = \frac{2\mathbf{H}}{R}. \qquad (19)$$

In the same manner as above, we find that the thermodyn. potential has the same value in the homogeneous phase of the liquid as in that of the vapour. If A and C in fig. 6 are the points of the theoretical isotherm, which correspond respectively with the volumes of the liquid and vapour, which limits the capillary layer, we must have thus:

surface DASQ=surface SCKH.

The gradient of the hydrostatic pressure  $p_1$  normal to the surfaces of equal density may be deduced from the equation (16), when we change R into -R. Hence

$$\frac{dp_1}{dh} = -\frac{2(p_1 - p_2)}{R}. \qquad (20)^*$$



The departure from the law of Laplace or the difference  $p_1-p_2=\frac{1}{4\pi f}\left(\frac{d\mathbf{V}}{dh}\right)^2$  being positive, the gradient  $\frac{dp_1}{dh}$  is always negative. That the  $p_1-v$ -curve has a point of inflexion may be demonstrated in the same manner as above in the case of a capillary layer, which envelops a spherical bubble of vapour. Integrating (20) we have the well-known equation of Lord Kelvin:

$$p_v - p_l = -\frac{2H}{R}$$
.

The  $p_2-v$ -curve may be studied in the same manner as above.

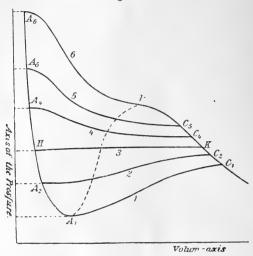
# § 5. The physical meaning of the unstable part of the Isotherm of James Thomson.

We will now firstly resume the considerations with regard to the  $p_1-v$ -curves in *one* figure. In the case that the vapour envelops the capillary layer, and that therefore the liquid is in the interior of the capillary layer, the maximum value of the pressure  $p_v$  in the vapour corresponds with the

\* This equation is the same as the relation (17). Above we have found this equation as a particular case of the more general relation (16a).

point P in fig. 2 or fig. 6; while in the case that the capillary layer is enveloped by the liquid, the *minimum* value of the pressure  $p_l$  in the liquid is given by the point G in figs. 2 and 6. We get, therefore, for the complete set of  $p_1-v$ -curves the curves of fig. 7. The curve  $A_1$   $C_1$  corresponds to a vapour-bubble, for which the pressure in the





liquid, round about it, has a minimum value. The corresponding radius of the spherical vapour-bubble is given by the formula:

$$R_v = \frac{v_2 + v_2'}{v_2 + v_2' - (v_1 + v_1')} \frac{2H'}{p_1 - p_{\min}}, \quad . \quad . \quad (21)$$

where  $p_{\min} = p_l$  corresponds to the point  $A_1$ . Because the total departure of the law of Pascal has not necessarily reached already its maximum value, I have written H' instead of H, H presenting the maximum value of the surfacetension\*. In the following manner we may show that nevertheless H' is of the same order of greatness as H. For the temperature  $T = 0.844 T_k I$  have found † that the thickness

† Zeitschr. f. phys. Chem. li. pp. 358 & 361 (1905). In the Phil. Mag. for October 1907, p. 522, I have given for a temperature  $T=0.82T_k$ :

$$h = \frac{\text{surface-tension}}{\text{vapour-pressure}}$$
.

<sup>\*</sup> When, namely, the radius of the spherical vapour-bubble has a value of the same order as the sphere of action, or smaller, the surface-tension is a function of the radius.

h of a plane capillary layer may be expressed by

$$h = \frac{3H}{2\overline{p_1}},$$

where H is the ordinary constant of Laplace, and  $p_1$  the pressure of the vapour. If we accept the equation of state of van der Waals for the homogeneous phase, we have for this temperature\*

$$p_{\min} = 0$$
,

while the proportion between the specific volume  $v_2$  of the vapour and that of the liquid is about 19. Hence (see equation (19)):

$$R_v = \text{circa } \frac{19}{18} \cdot \frac{2H'}{p_1} = \frac{19}{18} \cdot \frac{2H'}{\frac{3H}{2h}} = \frac{4}{3} \cdot \frac{H'}{H} h.$$
 (22)

Now the radius of the bubble of vapour must be at least the average distance between two molecules, and because this distance has in the vapour a value of the order of the radius of the sphere of action, the cohesion of the vapour being practically null, we see that in the formula (22) the minimum value of  $R_v$  is of the same order as h, and H' must therefore be also of the same order of greatness as H, then h, the thickness of the capillary layer, is of the order of the sphere of action.

The curve  $A_6 C_6$  corresponds to the other limit. The radius of the corresponding spherical drop of liquid is given by the formula:

$$R_{l} = \frac{v_{1} + v_{1}^{"}}{v_{2} + v_{2}^{"} - (v_{1} + v_{1}^{"})} \frac{2H''}{p_{\text{max.}} - p_{1}}.$$
 (23)

 $\mathrm{H}^{\prime\prime}$  denotes the departure from the law of Pascal,  $v_1$  and  $v_2$  are respectively the abscissa of H and K in fig. 7, and  $v_1^{\prime\prime}$  and  $v_2^{\prime\prime}$  the abscissa of  $\mathrm{A}_6$  and P. If the radius of the spherical drop of liquid has a measurable value we have:  $\mathrm{H}^{\prime\prime}=\mathrm{H}$ .

Every point of the part PK (fig. 7) of the theoretical isotherm we have thus brought in connexion with a spherical drop of liquid. If  $C_5$  is the considered point, the ordinate and the abscissa of this point give respectively the pressure  $p_v$  of the vapour which surrounds the drop and the reciprocal value of the density of the vapour. The pressure  $p_l$  of the liquid in the interior of the drop is given by the ordinate of  $A_5$ , for which the thermodynamical potential has the same

value as for the point  $C_5$ . The reciprocal value of the density of the drop is given by the abscissa of  $A_5$ . A conformable consideration we may make for each pair of points below the part HK of the empiric isotherm. If, for instance, in the points  $A_2$  and  $C_2$  the thermodynamic potential has the same value, these points determine the state of a spherical bubble of vapour and of the liquid which surrounds the bubble. In the same manner we have found above, that a pair of points above the part HK of the empiric isotherm determine the state

of a spherical drop of liquid with its vapour.

A part of the theoretical isotherm that we, however, have not considered hitherto is the part A<sub>1</sub>P (fig. 7). This part of the isotherm corresponds, as everyone knows, with the phases, which cannot be realized under uniform pressure, because the pressure would be increased with the increase of the volume. Therefore Maxwell says in his text-book 'Theory of Heat': "We cannot, therefore, expect any experimental evidence of the existence of this part of the curve, unless, as Prof. J. Thomson suggests, this state of things may exist in some part of the thin superficial stratum of transition from a liquid to its own gas, in which the phenomena of capillarity take place."

Now the curve AEC in fig. 5 presents the relation between half the sum of the maximum and minimum value of the

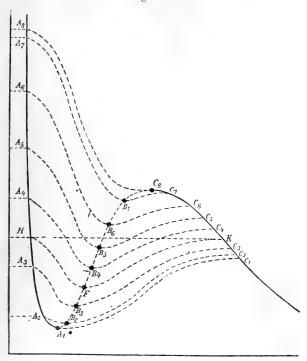
pressure  $\left\{\frac{p_1+p_2}{2}=\mathfrak{p}\right\}$  in every point of the capillary layer

and the reciprocal value of the density in this point, and, as I have demonstrated above, the point E on the curve AEC, where the ordinate has its minimum value, and where the thermodynamical potential has the same value as in the homogeneous phases of the liquid and the vapour (the corresponding points are A and C) lies exactly on the theoretical isotherm. Therefore we have the following theorem:

Every pair of points of the isotherm, for which the thermodynamical potential has the same value (fig. 8) (as A<sub>8</sub> and C<sub>8</sub>, A<sub>7</sub> and C<sub>7</sub> &c.), corresponds above the rectilinear part HK of the empiric isotherm to a spherical drop of liquid, such, that the state in the interior of the drop and the state of the vapour, which surrounds it, is determined in a singular manner by the situation of this pair of points. In the same manner, every pair of points below the rectilinear part HK of the empiric isotherm (A<sub>3</sub> and C<sub>3</sub>, A<sub>2</sub> and C<sub>2</sub>, &c.), for which the thermodynamical potential has the same value, corresponds to a spherical bubble of vapour. If we now construct the curves, such as A<sub>6</sub>B<sub>6</sub>C<sub>6</sub>, A<sub>3</sub>B<sub>3</sub>C<sub>3</sub>, &c., which present the relation between

half the sum  $\mathfrak{p} = \frac{p_1 + p_2}{2}$  of the maximum and minimum pressure and the reciprocal value of the density for every point of the

Fig. 8.



capillary layers, which envelops the spherical drops and the spherical vapour-bubbles, the minima of these curves present exactly the unstable part  $A_1FB_6C_8$  of the theoretical isotherm of James Thomson.

The densities of the unstable phases of the isotherm are thus present in the considered capillary layers under a system of pressures, which are dependent on the direction, the maximum and minimum values of these pressures being respectively in the direction of the lines of forces and perpendicular to the latter. The theorem above gives thus the physical meaning of the unstable part of the theoretical isotherm of James Thomson.

XLII. On the Heating Effects produced by Röntgen Rays in Lead and Zinc. By H. A. Bumstead, Ph.D., Professor of Physics, Yale University \*.

IN an earlier number of this Journal † the writer described a series of experiments, from which it appeared that, when Röntgen rays were equally absorbed in lead and in zinc, approximately twice as much heat was generated in the lead as in the zinc. These experiments were carried out in the Cavendish Laboratory of the University of Cambridge, and the further prosecution of the investigation was interrupted by the writer's return to America. An unusual pressure of other duties prevented the resumption of the work until last summer and autumn, when a considerable series of observations was made with such variations of the conditions as might be expected to reveal certain possible errors in the original experiments. It soon became apparent that errors had been present, and that the difference in the quantities of heat generated in the two metals was much less than had appeared from the earlier experiments. The source of the original mistake was inherent in the apparatus used (a special form of radiometer), and although it could be diminished it was not easy to eliminate it altogether: there still remained an uncertainty of from 5 to 10 per cent. as to the equality of the heat in the two metals. I had accordingly planned, before publishing this correction, to attempt to bring the result within narrower limits, by substituting for the radiometer, a thermopile, with which the principal source of difficulty could be easily avoided. In the meanwhile, however, a paper by E. Angerer has appeared ‡, in which a series of very careful experiments of this kind are Angerer's results leave no doubt, I think, that the heating effects in lead and zinc are equal to within a few per cent.; the total effect is so small and the experimental difficulties are so considerable, that it does not seem practical at present to seek for a possible small difference within these Certain facts in connexion with the emission of electrons by metals make it not improbable that there may be some liberation of atomic energy when ultra-violet light or Röntgen rays fall on a heavy metal. Such considerations have been advanced by Lenard S, by W. Wien |, and by

<sup>\*</sup> Communicated by the Author.
† Phil. Mag. February 1906, p. 292.
‡ Ann. der Phys. xxiv. p. 370 (1907).
§ Ann. der Phys. viii. p. 169 (1902).
|| Ibid. xviii. p. 991 (1905).

J. J. Thomson \*; and they are in a measure supported by the recent work of Bestelmeyer †, Cooksey ‡, and Innes §. But so little is as yet known about the mechanism of this emission of electrons, that it is by no means certain that the facts observed by these investigators necessarily involve the liberation of atomic energy. And in any event, the results of Angerer indicate that this energy, if it is set free, forms only a small part of the total produced by the absorption of Röntgen rays.

The source of my own erroneous results was found in the greater rate of loss of heat by the zinc, for a given temperature above its surroundings, than by the lead. In the original experiments small strips of the two metals (of different thickness so as to produce equal absorption of the rays) were held by an ebonite support so that each strip was opposite one vane of a radiometer made of thin aluminiumfoil and suspended by a quartz-fibre. The whole was enclosed in a heavy metal case from which the air could be exhausted to the point of maximum radiometric-sensitiveness. aluminium window, with a movable lead screen outside, permitted either or both of the strips to be subjected to the action of Röntgen rays; and through a glass window the deflexions of the radiometer could be read by telescope and scale. The position of the strips could be reversed and the balance of the two vanes tested by a device which is described in the former paper. The repulsion of one of the vanes was of course primarily dependent on the temperature of the surface of the strip to which it was exposed; to make the radiometer deflexions a measure of the quantities of heat developed in the two metals, it was necessary that the rate at which the two metals lost heat, per degree excess of temperature above their surroundings, should be the same. If then the steady state was observed when the heat lost was equal to the heat generated, the rise in temperature of either strip would be proportional to the heat developed in it. I sought to realize this condition by covering both metals with thin aluminium-foil which was stuck to the metal by a very thin layer of wax. It was recognized that, if any considerable part of the total heat were lost over the supports to which the ends of the strips were attached, the zinc would be at a disadvantage in comparison with the lead owing to its greater conductivity and thickness.

<sup>\* &#</sup>x27;Conduction of Electricity through Gases,' p. 319.

<sup>†</sup> Ann. der Phys. xxii. p. 429 (1907). † Am. Jour. Sci. xxiv. p. 285 (1907).

<sup>§</sup> Proc. R. S. A. lxxix. p. 442 (1907).

possibility appeared to be excluded (as well as any sensible difference in the emissivity of the surfaces) by a control experiment in which the strips were heated by exposure to the light of an incandescent lamp, instead of Röntgen rays. The deflexions of the radiometer were almost exactly equal in this case, and the whole behaviour was such as to indicate that the conditions specified above were fulfilled; the question was discussed in the previous paper and the experiments with light were taken as excluding the possibility of the result being due to the more rapid loss of heat by the My recent experiments, however, force me to the conclusion that the zinc did lose heat more rapidly (for a given temperature) mainly over the supports, and that, in the control experiments, this was accidentally compensated by a greater absorption of the incident light by the zinc, possibly owing to a thinner layer of wax between it and its covering of aluminium-foil. The experiments with light were made at the very end of my stay in Cambridge and could not be repeated on account of lack of time: if they had been repeated under slightly varied conditions, the error would doubtless have been discovered. The agreement between the two metals, however, was so good, and the improbability of two unrelated large errors which exactly compensated each other was so great, that I was led to put more confidence in this result than it deserved.

When the experiments were again taken up, however, I did consider the possibility that the emissivity of a surface and its absorption of light might vary together—thus destroying the force of the control experiment. It was not likely that the emissive power of a surface for low temperature radiations would be proportional to its absorption of the high temperature radiation from an incandescent filament, but I nevertheless made some experiments to test the For this purpose two lead strips were used, one of which was left with its original dull surface and the other covered with aluminium-foil. Röntgen rays and light were both used: the rays gave deflexions agreeing to about 5 per cent.; with light, on the other hand, the dull lead strip gave four times the deflexion of the other. It thus appeared (as was expected) that the rate at which heat was lost varied very little with the state of the surface, while the absorption of light varied greatly. Thus there appeared to be no reason

for distrusting the control experiment.

A series of experiments was next made, by means of an electroscope, on the amount of secondary radiation from lead and zinc, in order to test the possibility that a considerable

fraction of the energy in the case of the zinc might escape in this form. It appeared from these that the total intensity of the secondary rays escaping from both surfaces of the zinc strip (as measured by the ionization produced) was less than

1/15 of the primary rays absorbed.

The energy measurements were again taken up, and a change was made in the method which would render it independent of the rate of loss of heat from the metals. The strips of lead and zinc were held at the ends by massive brass clamps, connected to binding screws outside the case by means of rods insulated from the case. In this way a known current of electricity could be sent through either strip; the resistances of the strips were measured, and thus a known quantity of the energy could be developed in either strip and the corresponding deflexion of the radiometer obtained. loss of heat through the electrodes was so rapid, however (especially in the case of the zinc), that measurable deflexions could not be got with the Röntgen rays. I accordingly substituted for each strip a five-barred grid, carefully cut from the same materials, each bar being one millimetre wide; one electrode-clamp held the beginning of the first bar, the other the end of the fifth bar, so that the current passed through the five bars in series. This served the purpose although the deflexions produced by the rays falling on the zinc were still too small for very accurate measurement. The resistance of the zinc grid was  $6.5 \times 10^{-5}$  ohm and of the lead  $64 \times 10^{-5}$  ohm; currents of 10 to 12 milliamperes were used in the lead and from 35 to 50 milliamperes in the The deflexions produced by either grid were found to be proportional to the quantity of heat developed in it, but the sensitiveness of the two grids was very different. Thus in one experiment which may serve as an example of many which were made, the energy necessary to produce a deflexion of 1 cm. was: -with the zinc grid, 26.8 ergs per second; with the lead grid, 7.82 ergs per second. When the Röntgen rays fell upon the zinc, the deflexion of the radiometer was 2.6 cm.; when on the lead, 10.8 cm. measurements give 70 ergs per second in the zinc and 84 ergs per second in the lead; the ratio of the two is 1.2. This is a much smaller difference than was obtained in the Cambridge experiments; and, what is more significant, any errors (due, for example, to a gain of heat by both strips from other portions of the apparatus struck by the rays, or to imperfect screening of one strip) would favour the lead on account of its greater sensitiveness. So that the difference would be less than 20 per cent. rather than more.

A more careful consideration of the conditions of the original experiments showed that it was not impossible that the result obtained was due to escape of heat by conduction through the ebonite disk which supported the strips, the aluminium leaf which covered the disk (to prevent electrical effects), and the copper wires by which the strips were earthed. The lead strips had also between them and the disk pieces of cardboard to bring their front surfaces into the same plane with those of the thicker zinc strips. I accordingly repeated the experiments with the following modifications: the cardboard was left out and the zinc strips sunk into recesses cut in the disk: the aluminium-foil was scraped away from the vicinity of the ends of the strips; and the strips were earthed by manganin wires 0.05 mm. in diameter and 3 cm. long; also the strips were covered with aluminium paint instead of foil to make the coefficient of absorption for light less uncertain.

Two series of observations with this arrangement were made (one with Röntgen rays, the other with light), during which the balance of the radiometer vanes was tested, the position of the metals reversed and various corrections applied as detailed in the former paper. The ratio of the lead effect

to the zinc effect was:—

With Röntgen rays ......  $1.47 \pm .04$ , With light .....  $1.43 \pm .06$ .

These results show that the heating effects of Röntgen rays in the two metals are equal, with an uncertainty of between 5 and 10 per cent.

Some time before the above results were obtained, two experiments of another kind were made with the view of testing certain aspects of the hypothesis that Röntgen rays caused atomic disintegration. The first was an attempt to find out whether any rays similar to  $\alpha$ -rays existed among the secondary radiations given off when a heavy metal is exposed to Röntgen rays. An iron tube was provided with an aluminium window at the side, through which a beam of Röntgen rays could be sent; this beam fell upon a lead plate at an angle of 45°. To the upper end of the tube, 3 cm. above the centre of the lead plate, was cemented a glass plate, the inner side of which was coated with powdered zincblende. The tube was exhausted to 0.1 mm. and the zincblende screen examined by means of a lens in the ordinary manner, while the rays fell on the lead plate. No scintillations were seen; the sensitiveness of the eye was tested by alternate observations of another similar screen placed above a weak radium preparation which gave a few scattered scintillations; this was placed near the Röntgen tube and observed while the tube was excited. A large Müller water-cooled tube was used (20 cm. in diameter) and a heavy discharge sent through it: the focus was only 28 cm. from the lead plate, so that the latter was exposed to very intense rays. The air between the lead and the screen would have formed at atmospheric pressure, a layer only 0.004 mm. thick.

I also tried to find out whether Röntgen rays had an accelerating effect upon the disintegration of a radioactive substance. The active deposit of thorium was used in preference to one of the more permanent radioactive substances. An aluminium plate, one side of which had been exposed to thorium emanation for some hours, was placed over a hole in the wall of an electroscope with the exposed side inward. A number of measurements of the activity were made and then the plate (without being removed) was exposed for ten minutes to strong Röntgen rays from the large bulb with its focus 20 cm. from the plate. The ionization was then measured again several times. The following is an example of the results obtained:—

Activity before exposure .....  $7.56 \pm .056$ Activity after exposure .....  $7.54 \pm .076$ 

Repetitions of the experiment gave similar results.

#### Conclusions.

1. The result previously obtained by the writer that the heat generated in lead by Röntgen rays was twice that in zinc is not confirmed by further experiments, which show that the quantities of heat are equal, with an uncertainty of from 5 to 10 per cent. The source of the error was imperfect heat-insulation of the metals; this escaped the control experiment on account of a difference in the coefficients of absorption of the surfaces for light, which, by an unfortunate accident, was just sufficient to compensate the other inequality.

2 No rays capable of producing scintillations on a zincblende screen are present among the secondary radiations

from lead when exposed to Röntgen rays.

3. The disintegration of the active deposit from thorium emanation is not hastened by exposure to Röntgen rays.

Sloane Laboratory, Yale University, New Haven, Conn., Dec. 6, 1907. XLIII. On the Frequencies of the Free Vibrations of Quasipermanent Systems of Electrons, and on the Explanation of Spectrum Lines. Part I. By G. A. Schott, B.A., B.Sc., University College of Wales, Aberystwyth\*.

§ 1. In a previous communication † I have shown that a ring of electrons, rotating in a field due to electrons, all of which exert only electromagnetic forces, has a praccally determinate radius and velocity, provided only each electron be expanding at a very slow rate, uniform or not. With the aid of expanding electrons we can build up a purely electromagnetic system possessing a determinate structure, and therefore also determinate free periods.

Secondly ‡ I have examined the waves emitted by a rotating ring of equidistant electrons, when disturbed from steady motion in any way, and have shown that of all the free vibrations, which can be excited in such a ring even by violent disturbances, only a few can produce waves sufficiently powerful to give observable spectrum-lines. It follows that only a small proportion of the free vibrations of a system of electrons can be used to account for spectrum-lines. In all probability a similar limitation exists for other vibrating systems; but as they do not so readily lend themselves to a calculation of relative intensities, it has hitherto escaped notice. It is indeed hardly conceivable that this difficulty is peculiar to systems of electrons.

§ 2. In order to account for known spectra we must study more complex systems of electrons; but if, for the present, we confine ourselves to quasi-permanent systems, that is to systems which can last for very many periods of vibration without appreciable change of structure, the problem is very much simplified. In fact such systems are necessarily built up of circular rings of equidistant electrons, relatively far apart, and each rotating with its own determinate velocity about a common axis. This may be seen as follows.

The electromagnetic field due to an electron which describes a closed orbit with period T can be expressed in the usual way in terms of a scalar potential  $\phi$  and vector potential A by the equations

$$\mathbf{E} = -\nabla \phi - \frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{H} = \text{curl } \mathbf{A}.$$

<sup>\*</sup> Communicated by the Author.
† Schott, Phil. Mag. [6] vol. xii. p. 21.
† Phil. Mag. [6] vol. xiii. p. 189.

At a distance from the electron large compared with its radius

a distance from the electron large compared with its
$$\phi = \sum_{j=-\infty}^{j=\infty} \frac{e}{T} \int_0^T \frac{1}{R} \cos \frac{2\pi j}{T} \left( t - \frac{R}{c} - t' \right) dt',$$

$$\mathbf{A} = \sum_{j=-\infty}^{j=\infty} \frac{e}{T} \int_0^T \frac{\mathbf{u}}{eR} \cos \frac{2\pi j}{T} \left( t - \frac{R}{c} - t' \right) dt',$$
(1)

where R is measured from the position of the electron at time t', and **u** is its velocity at that time.

$$R = \sqrt{(x-x')^2 + (y-y')^2 + (z-z')^2},$$

where the coordinates (x', y', z') of the electron are assigned functions of t' of period T.

The electric and magnetic forces due to a single electron thus consist of series of harmonic terms, no member of which in general is missing. The energy radiated away is therefore very considerable, and the motion can only be permanent for a very small velocity. We know from Earnshaw's Theorem that systems of discrete electric charges at rest are unstable: in general a minimum velocity is necessary for stability, but this is usually inconsistent with permanence. Hence we conclude that a system including stray electrons, each describing its own orbit independently of the others, is not permanent and stable. Ultimately these electrons either escape from the system or combine into groups, describing the same orbits.

§ 3. In order that a group may be quasi-permanent a number of the harmonic terms in the forces due to its several electrons must annul each other by interference. The condition for this is easily seen to be, that the coordinates of the ith electron of the group be given by equations of the form

$$x_i' = f\left(t' + \frac{iT}{n}\right), \quad y_i' = g\left(t' + \frac{iT}{n}\right), \quad z_i' = h\left(t' + \frac{iT}{n}\right).$$

The potentials then reduce to series of the form

$$\phi = \sum_{s=-\infty}^{s=\infty} \frac{ne}{T} \int_0^T \frac{1}{R} \cos \frac{2\pi ns}{T} \left( t - \frac{R}{c} - t' \right) dt', \quad . \quad . \quad (2)$$

where R is now measured from any one of the n electrons. The first n-1 periodic terms are now missing from the potentials; the largest periodic term left is that given by s=1, or by j=n.

§ 4. A similar interference occurs when the field is that

due to waves of small amplitude travelling round the ring. When the displacements of the *i*th electron, measured from its position in the quasi-permanent motion, are proportional to the real part of  $\exp\left[-\kappa t + \sqrt{-1}\cdot\left(qt - k\frac{2\pi i}{\pi}\right)\right]$ , the forces of the field consist of an infinite series of harmonic terms, the frequencies of which are  $q + \frac{2\pi(k+sn)}{T}$ , where s

takes all integral values from  $-\infty$  to  $+\infty$ ; of these the most intense are given by s=0, and to these the radiation of energy is almost entirely due. For the case of a circular orbit the rate at which energy is lost by radiation through

the sth harmonic is relatively of order  $J_{2m}\!\!\left(\!rac{4\pi
ho}{\lambda}\!\right)\!\!$ , where ho is

the radius of the orbit,  $\lambda$  the wave-length of the harmonic, and m=k+sn. For the harmonics m=0,  $m=\pm 1$ , the order is about the same; for greater values of m it is much less, diminishing, as m increases, faster than a geometrical pro-

gression whose ratio is  $\left(\frac{2\pi\rho}{\lambda}\right)^2$ , that is, about 1:1,000,000

For the general case the intensities have not been worked out, but there is every reason for expecting essentially the same result. We conclude that in general any disturbance of allowable amplitude (not greater than the distance between neighbouring electrons), for which  $k=0, \pm 1$ , gives rise to

appreciable radiation.

§ 5. Let us now consider a system of rings or groups of electrons. As we have seen, each ring, on account of its permanent motion, emits waves which disturb the other rings; and similarly is disturbed by them. It executes forced vibrations and radiates energy. If the system be a solitary one, the whole of this energy is lost to it, and hence the system cannot be permanent; but if the structure is such that the forced vibrations of each ring correspond to values k other than the values  $0, \pm 1, \ldots$ , the loss of energy is small, and the system is nearly permanent. We must bear in mind that for spectroscopic purposes an absolutely permanent system is not necessary; it is sufficient if we account for the degree of homogeneity and the fineness of spectrum-lines as we know them. Lummer and Gehrcke estimate that interference with one million wave-lengths difference of path can be realized with the red cadmium line. Further, the width of this line when at its finest is of the order ·01 A.U., of which the greater part is perhaps due to Doppler effect;

let us assume a width of one millionth of a wave-length in round numbers. Then we may say, that if the red cadmium line be due to one of the free vibrations of a system of rings of electrons, the structure of the system, as determined by the velocities of its rings, can alter by as much as one millionth during the emission of the line, that is during one million periods; otherwise the line would be broader than is really is. Thus the greatest change of velocity consistent with the observed homogeneity and fineness of spectrum-lines is of the order  $10^{-12}$  in one period of the red cadmium line, that is in  $2 \cdot 10^{-15}$  second; in all probability it is much smaller. The perturbations admissible in our system of rings must be consistent with this upper limit, that is, the rate of loss of energy caused by them must be less than  $10^{-12}$  of the

energy of the system in one period.

§ 6. It is to be noted that the rate of change of structure just calculated is the greatest possible consistent with observation. If we assume that it actually exists, we thereby make a special hypothesis as to the emission of spectrumlines. For the loss of energy implies a diminution of the orbital velocities of the rings of electrons, and a corresponding diminution of the free periods of the system. When the system begins to radiate it emits the most refrangible part of the line, the light emitted becomes gradually less and less refrangible, and after one million vibrations or so the emission ceases entirely. The system cannot again emit red cadmium light until by some external agency its internal energy has been restored to its original value. Thus we are compelled to suppose (1) that only a fraction of all the atoms in a radiating gas at any instant emit any one spectrum-line; (2) that the atoms begin to emit red cadmium light, and only begin to do so, when their internal energy reaches a perfectly determinate upper limit, and cease to do so when it falls to a certain lower limit; while they emit no energy whatever for a considerable range outside these limits. There is sufficient evidence in favour of the first supposition to make it appear reasonable: but it is so difficult to construct a mechanism in accordance with the second, that for the present we shall assume the radiation from our system to be much smaller than the limit just calculated.

§ 7. The question now arises: What types of groupings of electrons, and what arrangements of groups are consistent with small radiation, implying the absence of all perturbations

for which k=0, +1?

Let us consider the field due to a circular ring, which is of course given by the general expression (2). In this case,

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using polar coordinates, we may write

$$R = \sqrt{r^2 + r'^2 - 2rr'\sin\theta\cos(\phi' - \phi)},$$

with r' = constant,  $\phi' = \omega t' + \delta$ , and easily find on changing the variable of integration from t' to  $\chi = \phi' - \phi$ ,

$$\phi = \sum_{s=-\infty}^{s=\infty} \frac{ne}{2\pi} \int_{0}^{2a} \frac{1}{R} \cos ns \left(\omega t + \delta - \phi - \frac{\omega R}{c} - \chi\right) d\chi$$

$$= \sum_{s=-\infty}^{s=\infty} \frac{ne}{\pi} \cos ns \left(\omega t + \delta - \phi\right) \int_{0}^{\pi} \frac{\cos \left(ns\omega R/c\right)}{R} \cos \chi d\chi$$

$$+ \sum_{s=-\infty}^{s=\infty} \frac{ne}{\pi} \sin ns \left(\omega t + \delta - \phi\right) \int_{0}^{\pi} \frac{\sin \left(ns\omega R/c\right)}{R} \cos \chi d\chi, \quad (3)$$
where  $R = \sqrt{r^{2} + r'^{2} - 2rr'} \sin \theta \cos \chi.$ 

Thus t occurs only in the circular functions, so long as we are dealing with a fixed point  $(r, \theta, \phi)$ . To find the mechanical force on an electron we differentiate as usual with respect to the coordinates  $(r, \theta, \phi)$  and the time (t), as the case may be. When the electron is moving, the coordinates are given functions of t; but these values of the coordinates as functions of t are only to be substituted after all the differentiations necessary in deriving the forces have been performed.

§ 8. When the electron in question belongs to a second circular ring of n' electrons, rotating with angular velocity  $\omega'$  about the same axis as the first, we substitute  $\phi = \omega' t + \delta' + \frac{2\pi i}{n'}$ , and thus find for the potentials and forces series of harmonic terms of the form  $\cos_{\sin ns} \left\{ (\omega - \omega')t - \frac{2\pi i}{n'} \right\}$ . The perturbations produced are of the same type, which is obviously

bations produced are of the same type, which is obviously that of § 4 with  $\kappa = 0$ ,  $q = ns(\omega - \omega')$ , k = ns; and the emitted waves are given by m = ns + n's', where s' is any positive or negative integer. The radiation is small provided ns + n's' cannot take the values  $0, \pm 1$ , zero values of s, s' being omitted, since they imply zero frequency and no variety at all.

It is at once obvious that the values  $0, \pm 1$  will occur; if n, n' be incommensurable, and  $\frac{P}{Q}$  be the last convergent to  $\frac{n}{n'}$ , we need only make s=n', s'=-n to get m=0, and  $s=\pm Q$ ,  $s'=\mp P$  to get  $m=\pm 1$ . Thus we cannot entirely avoid the dangerous harmonics in question.

We can, however, ensure that their amplitudes are small.

For generally the coefficients of high harmonics in (3) are small provided the rings be not close together; and it is sufficient if either s or s' be a large number when the rings are fairly near together, smaller when far apart. This condition can always be satisfied, except for special values of n, n'.

§ 9. When the electron belongs to a ring which has not the same axis as the first, the coordinates r and  $\theta$ , as well as  $\phi$ , involve t, and so also do the coefficients of the circular functions in (3). Expanding them in Fourier's series we see that the mechanical force on the moving electron now involves harmonics of all integral orders, and not merely of the orders  $n, 2n, 3n, \ldots$ . Consequently it is no longer possible by a suitable choice of the values of n, n', to ensure that the amplitudes are very small for the dangerous vibrations for which  $m=0, \pm 1$ . Hence considerable radiation occurs, and the system is not permanent. A fortiori the same thing occurs when the rings are not circular and are oriented in an arbitrary manner.

We conclude that no system of electrons can be permanent unless its electrons be grouped in circular rings of equidistant

electrons, all rotating about the same axis.

§ 10. This conclusion can be at once extended to a system, which is not solitary, as we have hitherto supposed, but is surrounded by a large number of other systems, just as an atom in a radiating gas is surrounded by a very large number of other atoms. It is true that the energy emitted by the system, or atom, in this case is, at any rate in part, replaced by energy absorbed by it from the field due to the surrounding systems, or atoms, and that to an amount depending on the absorptive index of the gas for its own radiations. But the observations on the degree of homogeneity and the fineness of spectrum-lines, on which the conclusion of § 9 has been based, themselves apply to a complex of atoms, and not to a solitary atom.

In the same way measurements, such as those of E. Wiedemann, of the amount of energy radiated per second from a flame or other source, enable us to calculate the net loss of energy of an atom due to radiation, that is, the excess of the amount emitted above the amount absorbed. If the absorption be considerable and be neglected, the net loss is still correctly estimated on the average; but since in the case of large absorption the energy actually radiated by the flame comes from a thin surface layer only, the amount of energy emitted from a single atom, and the net loss of each surface atom, are both underestimated. Since in this case the observed spectrum-lines are due to the surface layer alone, and the

radiation from its atoms is underestimated, the argument of

§ 9 is rendered all the more cogent.

§ 11. We shall now examine the frequency equations of a ring of the quasi-permanent system of § 9, in order to form an estimate of the frequencies to be expected from a system whose scale is comparable with that of an atom. Estimates of this kind are frequently omitted on the ground that they are illusory, because the dimensions of an atom are not sufficiently well known. However, in the present state of knowledge this criticism is not quite justifiable; and besides we merely require superior limits for our purpose. Such quantities as the number of molecules in 1 c.c. of gas under normal conditions (4.1019), the mass of the atom of hydrogen (10<sup>-24</sup> gr.), and the diameter of a molecule (at most from  $10^{-8}$  to  $10^{-7}$  cm., probably nearer the lower limit), have been calculated by various methods with consistent results, and are sufficiently well established to make estimates of frequencies and wave-lengths of considerable use in judging the merits of a proposed model of an atom. We should have considerable hesitation in accepting as a working model a system whose wave-lengths were very different from those of light-waves.

§ 12. This is the proper place to notice a fundamental difference between systems of electrons in orbital motion and systems built up of Hertzian vibrators or of elastic bodies. Systems of the latter types of different linear dimensions, but otherwise similar, have their wave-lengths in the ratio of their linear dimensions. Now, speaking roughly, wave-lengths of lightwaves are a thousand times as great as the linear dimensions of the atom; therefore the wave-lengths of the free vibrations of the Hertzian, or of the elastic, system must be roughly one thousand times its linear dimensions, in order to furnish a satisfactory atomic model. Obviously simple vibrators, spheres, ellipsoids, rods and the like, do not satisfy this condition, so that special assumptions are necessary; for example, a suitable Hertzian vibrator might consist of two conductors so close together as to have a capacity one million times the

linear dimensions of the system.

On the other hand, a ring of electrons involves three linear quantities in its specification, namely the radius of the ring, and the radii of the negative and positive electrons, of which the two latter remain the same when the linear dimensions of the system are altered. For this reason the wave-lengths of the free vibrations of the ring are in no direct relation to the radius of the ring; in fact it may happen that a very small ring emits longer waves than a large one. The size of

the ring must be considered in every calculation of the ratio

of the wave-length to the radius.

§ 13. We shall now study the frequency vibrations of a circular ring of equidistant electrons, which forms part of a system of rings of the type specified in § 9, with a view to estimating the wave-lengths, and comparing them with those of light-waves. For this purpose it is not necessary to prove that the system is stable; it is sufficient to assume its stability and permanence. If it be found that a sufficient number of wave-lengths are comparable with those of lightwaves to account for a reasonably large number of spectrumlines, we may accept the system provisionally as a satisfactory model and examine its stability; if not, it must be rejected, whether stable or not, as by itself incapable of accounting for spectra by means of its free vibrations. If no system be found which satisfies all these conditions by itself, we need not necessarily reject the electron models as useless; for we never have to deal with isolated atoms of any element, but only with the element in bulk. It is quite possible that the emission of spectra, as we know them, is a property of complexes of atoms, and not of the individual atom.

§ 14. We shall for the sake of simplicity begin with the study of the models proposed by Nagaoka and by J. J. Thomson, in which no account is taken of those terms in the frequency equations, which are due to radiation, an omission implying velocities small compared with that of light. We shall then extend our investigations to the general case, where the effects of radiation are taken into account, and no special hypothesis is made as to the nature of the field

in which the ring moves.

Before proceeding to the study of special systems we shall mention a few points which concern all systems equally.

Notation.

Number of electrons in the ring =n.

Radius of the ring  $= \rho$ .

Angular velocity  $=\omega$ .

Velocity of light = C.

Velocity of electron/velocity of light  $=\omega\rho/C=\beta$ .

The azimuth at time t of the ith electron is given by

$$\phi = \omega t + \delta + \frac{2\pi i}{n}$$
;

its coordinates in steady motion by

 $x = \rho \cos \phi$ ,  $y = \rho \sin \phi$ , z = 0. Phil. Mag. S. 6. Vol. 15. No. 88. April 1908.

 $2~\mathrm{H}$ 

When the ring is slightly disturbed from steady motion the displacements of the ith electron, in the direction of motion, towards the centre and parallel to the axis, are denoted by  $(\xi, \eta, \zeta)$ ; they are measured from the position which the electron would have occupied at the same time in the steady motion, not from a point fixed in space. Thus when disturbed the coordinates of the electron are

$$x = (\rho - \eta) \cos (\phi + \xi/\rho), \quad y = (\rho - \eta) \sin (\phi + \xi/\rho), \quad z = \zeta$$

Squares and products of the displacement are neglected in the equations of vibration (not of course in the energy).

This is substantially the method of representation used by Maxwell in his paper on Saturn's Rings, and by Nagaoka

and J. J. Thomson in their investigations.

§ 15. We may resolve the disturbance  $(\xi, \eta, \zeta)$  into a series of harmonic components proportional to terms of the form exp.  $\iota(pt-k\frac{2\pi i}{n})$ , where k is an integer, and p is a

complex constant of the form  $q + \iota \kappa$ .

This harmonic represents a wave with 2k nodes and 2kloops, travelling round the ring with angular velocity q/krelative to the rotating ring; for, apart from the damping factor, the displacements are unaltered when we increase i by n, and t by  $2\pi k/q$ . The angular velocity of the wave relative to fixed space is  $\omega + q/k$ ; accordingly q is the frequency relative to the rotating ring, as it appears to an observer revolving with it;  $q + k\omega$  is the frequency relative to fixed space, as it appears to a stationary observer. We may speak of q as the relative frequency, of  $q + k\omega$  as the absolute frequency, or the frequency simply.

Accordingly we notice that the waves emitted by the disturbed ring into the surrounding medium on account of the disturbance (q, k), consist of a series of simple harmonic waves with frequencies given by the formula  $q + (k + sn)\omega$ ,

s any integer ( $\S$  4).

It is obvious that we can obtain all the different types of disturbance possible, either by giving k every integral value and making s=0, or more conveniently, by giving k n independent integral values, and s all values in turn. We shall select the values

$$k = -\frac{n-2}{2}, \quad -\frac{n-4}{2}, \dots -1, \ 0, \ +1, \dots \ +\frac{n-2}{2}, \quad +\frac{n}{2}, \text{ when } n \text{ is even,}$$

$$k = -\frac{n-1}{2}, \quad -\frac{n-3}{2}, \dots -1, \ 0, \ +1, \dots +\frac{n-3}{2}, \quad +\frac{n-1}{2}, \text{ when } n \text{ is odd.}$$

In this case the harmonic s=0 is, for each value of k, by

far the most important (§ 4).

The distinction drawn between relative and absolute frequencies is vital, and is particularly insisted on by Maxwell; it is necessary again to insist on it since it is often overlooked. In fact the results of Nagaoka as to the arrangement of the relative frequencies of his ring in bands and series, for this reason do not apply to the frequencies of the waves emitted by his ring, and thus have no direct application to spectrum series.

§ 16. We must now consider the velocity of the ring, remembering that the ring cannot have a determinate structure and determinate free periods unless its velocity is determinate. In order to account for the determinateness of the wave-lengths of spectrum-lines, we must make one or other of two hypotheses; either:—

(A) Each system emitting lines has a definite structure; or

(B) The determinateness of wave-length is due to some action between the several systems, which constitute the radiating gas, in virtue of which only those waves which have definite frequencies ever become intense enough to produce observable lines. In this case each constituent system can be continually changing its structure within certain limits. All that is necessary is that the conditions for homogeneity and fineness of the lines satisfied (§ 9), so long as the system happens to be one of those which is producing a spectrum-line.

Although for obvious reasons the first hypothesis seems the more probable, the possibility that the second may be true cannot be left out of account entirely. All that it requires is that the system, during the emission of a spectrumline, be not altering its velocity by more than one 10<sup>-12</sup>th

part in one second (§ 5).

§ 17. The determinateness of structure necessary for hypothesis (A) can for a single ring only be obtained by means of expanding electrons (§ 1). For a system of rings it may be thought that the condition of permanence in spite of mutual perturbations of the rings, might alone suffice to fix the velocity of each ring within limits narrow enough to account for the observed tineness of spectrum-lines. But a closer examination of this question shows that in this way we can under no circumstances obtain conditions more than enough to fix the ratios of the velocities; and even then it is doubtful whether the limits can be drawn sufficiently close together to give sufficiently fine lines, assuming that the remaining condition can be otherwise obtained.

Jeans, it is true, obtains the required condition by introducing a hypothetical non-electromagnetic force between the electrons; this procedure amounts to giving up the simplicity which is the greatest advantage of the electron theory. But it has another disadvantage; it is of no use for a system in which the electrons are in orbital motion, and is in fact employed to avoid the necessity of orbital motions. In consequence it can only explain spectrum-lines by means of dynamical considerations, and gives the relation between the frequencies (N) of the lines in the form

$$N^2 = f(m), m \text{ an integer.}$$
 . . . (4)

To account for spectrum series we require the form

This fact led Lord Rayleigh to suggest that the numerical relation between the frequencies of a spectrum series is of a kinematical rather than a dynamical character; for it is by no means evident that the equation (4) can, by simple extraction of the square root, always be reduced to the form (4) in such a way as to agree with observed series to the accuracy required by experiment. The reduction has in fact been accomplished only in very special cases (cf. the model of W. Ritz\*).

Any system, on the other hand, which admits of the existence of orbital motions, for that very reason admits the possibility of a kinematical explanation of spectrum series, an advantage which ought not lightly to be given up. But every such system also requires the hypothesis of expanding electrons in order to completely fix its structure.

§ 18. I have stated elsewhere † that the rate of loss of energy due to radiation from a ring of electrons in steady motion is approximately equal to

$$R = \frac{Ce^2\beta^2}{\rho^2} \sqrt{\frac{n^5\gamma}{2\pi}} \exp 2n\left(\gamma - \frac{1}{2}\log\frac{1+\gamma}{1-\gamma}\right), \quad \gamma = \sqrt{1-\beta^2},$$

provided n be large; and to J. J. Thomson's value

$$R = \frac{2Ce^2}{\rho^2} \frac{n(n+1)(n\beta)^{2n+2}}{|2n+1|}$$

for small values of n, for which  $\beta$  also is small.

<sup>\*</sup> Ritz, Ann. Phys. (4) xii. p. 264. + Schott, Phil. Mag. [6] vol. xii. p. 22; vol. xiii. p. 194. One or two mistakes have corrected been here.

On the hypothesis of expanding electrons, the intrinsic electromagnetic energy of each electron of the ring diminishes

at the rate  $C^2\beta^2m\frac{\dot{a}}{a}$ , where a is the radius of the electron.

In consequence a tangential pull is exerted on each electron by the æther, due to the expansion, and a drag, due to the radiation; the velocity of the ring increases or decreases until the pull and drag balance. When this state is reached the radiation from the ring takes place at the expense of the intrinsic energy of its electrons; and we have

$$R = nC^2 \beta^2 m_a^{\dot{a}}$$

Hence we get

$$\sqrt{n^3\gamma}$$
 exp.  $2n\left(\gamma - \frac{1}{2}\log\frac{1+\gamma}{1-\gamma}\right) = \sqrt{2\pi}\frac{\mathrm{C}m\rho^2}{e^2}\frac{\dot{a}}{a} = \alpha$ , (6)

when n is large; and

$$\frac{n^2(n+1)}{|2n+1|}(n\beta)^{2n} = \frac{1}{2} \frac{Cm\rho^2}{e^2} \frac{\dot{a}}{a} = \frac{\alpha}{2\sqrt{2\pi}}, \quad . \quad . \quad (7)$$

when n is small.

§ 19. If we do not accept the hypothesis of an expanding electron, but adopt hypothesis (B), all we can assert is that the radiation R is at most at the rate of one  $10^{-12}$ th of the instantaneous kinetic energy, or thereabouts (§ 16).

The kinetic energy of the ring is of the order

$$\frac{1}{2}nC^2m\beta^2$$
.

Hence we get

$$R < 10^{-12} \cdot \frac{1}{2} nC^2 m \beta^2$$

$$\sqrt{n^3 \gamma}$$
. exp.  $2n \left( \gamma - \frac{1}{2} \log \frac{1+\gamma}{1-\gamma} \right) < \sqrt{\frac{\pi}{2}}$ .  $10^{-12} \cdot \frac{\text{Cm} \rho^2}{e^2} < \alpha'$ , (8)

when n is large; and

$$\frac{n^2(n+1)}{|2n+1|} (n\beta)^{2n} < \frac{1}{4} \cdot 10^{-12} \cdot \frac{Cm\rho^2}{e^2} < \frac{\alpha'}{2\sqrt{2\pi}}, \quad . \quad (9)$$

when n is small

We notice that the conditions (6), (7) and (8), (9) differ only by having a sign of equality replaced by one of inequality.

The quantity  $\frac{\text{C}m\rho^2}{e^2}$  changes as  $\beta$  changes, because both m and  $\rho$  change; its order is, however, easily assigned. In fact we may take  $e=3.5 \cdot 10^{-10}$  (E.S.U.),  $e/\text{C}m=1.9 \cdot 10^7$ ,  $\rho=10^{-8}$  cm. or thereabouts; so that  $\frac{\text{C}m\rho^2}{e^2}$  is of order  $1.5 \cdot 10^{-14}$ . Hence  $\alpha'$  is of the order  $2 \cdot 10^{-26}$ .

As to  $\dot{a}/a$ , we cannot well admit as possible a change in mass of the negative electron of as much as  $\frac{1}{3}$  per cent.

per annum: this makes  $\alpha$  of the order 4.10<sup>-24</sup>.

But a continual change in mass of the electron implies, on hypothesis (A), a secular change in wave-length of all spectrum-lines. A change of as much as 1/100 A.U. per annum could hardly escape detection; this is 1/600,000 of the wave-length for the D-lines. The corresponding relative rate per second is  $5 \cdot 10^{-13}$ ; taking this for the largest possible value of  $\dot{a}/a$  we find  $\alpha$  at most of order  $2 \cdot 10^{-26}$ .

We shall adopt  $2 \cdot 10^{-26}$  as the upper limit for both  $\alpha$  and  $\alpha'$ . It is considerably higher than the values used in my first paper. The following table gives the corresponding values of  $\beta$ . On the hypothesis of the expanding electron they are actual values for each ring, otherwise they are merely maximum values, in each case for the assigned value of  $\alpha$ .

n =	1.		2.		3.		4.			6.		7.		8.			10.
3=	10-1	3 2.	10-7	4.10	-5 3	6.10	-41	6.10	-3 3.9	9.10-	-3 8.1	. 10-	3 .0	14	022	2	031
n=	11.	12. 13	. 20	. 30.	40.	50.	60.	70.	80.	90.	100.	125.	150.	175.	200.	500.	1000.
β=	041 0	53 09	0 147	252	.333	.398	447	484	.518	.550	576	622	660	·691	714	·838	-897

We must particularly notice that, regarded as maximum values of  $\beta$  deduced from the observed degree of homogeneity and fineness of spectrum-lines (§ 5), these velocities have been calculated from the radiation R alone. Since the expression for R is calculated from the field at a great distance from the ring, the only assumptions made are those required by Maxwell's theory of the electromagnetic field. The table therefore gives maximum values quite independently of the forces assumed to act between the electrons at atomic distances; and is true for every model of the atom, which assumes the radiation to be electromagnetic, whether the forces between the electrons be purely electromagnetic or not.

Since  $\beta$ ,  $\gamma$  are less than unity and  $\gamma - \frac{1}{2} \log \frac{1+\gamma}{1-\gamma}$  is negative, the form of equations (6) to (9) shows that when we multiply  $\alpha$ , or  $\alpha'$ , by a power of 10, for a given value of  $\beta$  we diminish n by an amount nearly proportional to the exponent. For instance, if in § 5 we assume the breadth of a spectrumline to be 1 A.U., in place of '01 A.U., and the number of waves in a train to be 100,000 instead of 1,000,000, we must multiply  $\alpha'$  by  $10^3$  and diminish n by 10 per cent.

Physically speaking we see that a ring with a given velocity gives finer lines and longer wave-trains the greater the

number of electrons (of course only on hypothesis B).

§ 20. We shall here collect together certain results which occur in all the theories which we shall discuss. The notation is that of Maxwell in his paper on Saturn's Rings; we shall use it throughout for the sake of uniformity.

Neglecting  $\beta$ , the force exerted on any one electron of a ring of n equidistant electrons by the rest is a repulsion along

the radius equal to  $Ke^2/\rho^2$ , where

$$\mathbf{K} = \sum_{i=1}^{i=n-1} \frac{1}{4 \sin \left(\pi i / n\right)}.$$

For values of n equal to 10 or more  $K = \frac{n \log n}{2\pi}$  nearly.

When the ring is subject to a disturbance (q, k) parallel to the axis, to the same approximation the force on any one electron whose displacement is  $\zeta$  is in the direction  $\dot{\zeta}$  and equal to  $Je^2\zeta/\rho^3$ , where

$$J = \sum_{i=1}^{i=n-1} \frac{\sin^2(k\pi i/n)}{4\sin^3(\pi i/n)}.$$

When it is necessary to specify k we write  $J_k$  for J.

Obviously  $J_0=0$ , and  $J_1=K$ ; the maximum value of J occurs for  $k=\frac{n}{2}$ , or  $\frac{n-1}{2}$ , and for moderately large values of n is equal to  $0.017 \cdot n^3$  nearly.

When the ring is subject to a disturbance (q, k) in the plane of the orbit, with components  $(\xi, \eta)$ , to the same approxi-

mation the force in the direction & is

$$-\mathrm{N}e^2\xi/\rho^3+\iota\mathrm{M}e^2\eta/\rho^3,$$

and in the direction  $\eta$ ,

$$-\iota \mathrm{M} e^2 \xi/\rho^3 + \mathrm{L} e^2 \eta/\rho^3$$

452 Mr. G. A. Schott on Frequencies of Free Vibrations where as usual real parts alone are to be taken, and

$$\begin{split} & \mathbf{L} = \sum_{i=1}^{i=n-1} \left\{ \frac{\sin^2{(k\pi i/n)}}{4\sin^3{(\pi i/n)}} + \frac{\sin^2{(k\pi i/n)}}{4\sin{(\pi i/n)}} - \frac{1}{2\sin{(\pi i/n)}} \right\}, \\ & \mathbf{M} = \sum_{i=1}^{i=n-1} \frac{\sin{(2k\pi i/n)} \cdot \cos{(\pi i/n)}}{8\sin^2{(\pi i/n)}}, \\ & \mathbf{N} = \sum_{i=1}^{i=n-1} \left\{ \frac{\sin^2{(k\pi i/n)}}{2\sin^3{(\pi i/n)}} - \frac{\sin^2{(k\pi i/n)}}{4\sin{(\pi i/n)}} \right\}. \end{split}$$

Introducing another constant H, where

Herefore the constant H, where
$$H = \sum_{i=1}^{i=n-1} \frac{\sin^2(k\pi i/n)}{4\sin(\pi i/n)},$$

we may also write

$$L=J+H-2K$$
,  $N=2J-H$ .

With the same notation as before we have

$$\begin{split} & H_0\!=\!0, & H_1\!=\!\tfrac{1}{4}\cot\frac{\pi}{2n}, \\ & M_0\!=\!0, & M_1\!=\!K\!-\!\tfrac{1}{4}\cot\frac{\pi}{2n}, \\ & L_0\!=\!-2K, & L_1\!=\!\tfrac{1}{4}\cot\frac{\pi}{2n}-K, \\ & N_0\!=\!0, & N_1\!=\!2K\!-\!\tfrac{1}{4}\cot\frac{\pi}{2n}. \end{split}$$

H, L, N have their greatest values for  $k = \frac{n}{2}$ , or  $\frac{n-1}{2}$ ; for I moderately large values of n they are respectively  $\frac{1}{2}$  K,  $0.017.n^3$ ,  $0.034.n^3$ .

M has a minimum for  $k = \frac{n}{2}$ , or  $\frac{n-1}{2}$ .

The constants H, J, L, N are even functions of K, while M is an odd function.

We note the useful series

$$\begin{split} & \underset{s=0}{\overset{s=k-1}{=}} \frac{1}{4} \cot \frac{(2s+1)\pi}{2n}, \\ & \underset{s=0}{\overset{s=k-1}{=}} \frac{1}{2} (k-s-\frac{1}{2}) \cot \frac{(2s+1)\pi}{2n}, \\ & \underset{s=0}{\overset{s=k-1}{=}} \frac{1}{2} (k-s)(k-s-1) \cot \frac{(2s+1)\pi}{2n}. \end{split}$$

§ 21. Nagaoka's model \*.

The model consists of three parts:

(1) The ring of n equidistant negative electrons each of charge e and mass m.

(2) A central positive charge  $\nu e$  of mass M. To ensure the limited stability required by § 5,  $\nu$  must be very large

compared with n.

(3) A swarm of negative electrons sufficient to make the system neutral on the whole. According to § 9 permanence requires them to be grouped in rings coaxial with the ring (1). Stray electrons will either escape from the system, to be shortly replaced by others, or will owing to radiation lose their kinetic energy and coalesce to form rings, or join rings already present. Since the system cannot long remain charged without attracting negative electrons, when it is positive, and repelling them, when it is negative, it must on the average during its existence be very nearly neutral.

Nagaoka considers it likely that his system forms a flat disk or ring, all the negative electrons crowding towards the invariable plane. He appears to assume that the system as a whole can be permanent; but there appears to be some doubt, whether a flat disk or ring of many electrons moving with such small velocities as are necessary for permanence, under the influence of forces acting inversely as the distance,

can be stable at all †.

§ 22. It must be noted that in deriving his results Nagaoka neglects the field due to the swarm of negative electrons (3). This is strictly correct when the swarm forms an elliptic homeoid completely enclosing the ring; but Nagaoka considers it more probable that it forms a flat ring, approximately in the plane of the ring (1). The total charge of the swarm is that of  $\nu=n$  negative electrons, the whole system being neutral, and is herefore comparable in magnitude with the central positive charge. Hence its action cannot be neglected without further investigation. In order to form same idea of its effect we may treat it as an elliptic cylinder of the same cross-section, the long axis of the section lying in the plane of the ring.

Let the long axis of the section be 2a, the mean radius of the swarm c, the short axis negligibly small. We easily find for the radial force on a negative electron, at a distance  $\rho$  from the axis in the plane of the ring, a repulsion from the mean line (c) of the swarm, which inside the swarm is equal to

<sup>\*</sup> Nagaoka, Phil. Mag. [6] vol. vii. p. 445; Tokyo Proc. vol. ii. nos. 17-21. Schott, Phil. Mag. [6] vol. viii. p. 384.
† Pellat, Comptes Rendus, March 4 and April 8, 1907.

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$$\frac{2(\nu-n)e^2}{ca}\frac{c\sim\rho}{a}$$
, and outside is equal to  $\frac{2(\nu-n)e^2}{c(c\sim\rho+\sqrt{(c\sim\rho)^2-a^2})}$ 

The radial force due to the central charge being  $\frac{\nu e^2}{\rho^2}$ , the action of the swarm is only negligible when its mean radius (c) is large compared with the radius ( $\rho$ ) of the ring.

§ 23. On the assumption that the velocities are small enough to allow us to neglect the effects of radiation, we

find :—

(1) for the equation of steady motion,

(2) for the frequency equation for axial vibrations,

(3) for the frequency equation for orbital vibrations,

$$p^{4}-p^{2}\left\{\omega^{2}+\frac{(N-L-2K)e^{2}}{m\rho^{3}}\right\}+4p\omega\frac{Me^{2}}{m\rho^{3}}$$
$$-\frac{Ne^{2}}{m\rho^{3}}\left\{3\omega^{2}+\frac{(L+2K)e^{2}}{m\rho^{3}}\right\}-\left(\frac{Me^{2}}{m\rho^{2}}\right)^{2}=0. \quad (12)$$

By means of (10) equations (11) and (12) may be written in the forms

$$\frac{p^{2}}{\omega^{2}} = \frac{\nu - J}{\nu - K}; \qquad (13)$$

$$\frac{p^{4}}{\omega^{4}} - \frac{p^{2}}{\omega^{2}} \left( 1 + \frac{N - L - 2K}{\nu - K} \right) + \frac{p}{\omega} \frac{4M}{\nu - K}$$

$$- \frac{3N}{\nu - K} - \frac{N(L + 2K) + M^{2}}{(\nu - K)^{2}} = 0. \qquad (14)$$

These equations no longer involve  $\rho$  explicitly, and the coefficients of  $\frac{p}{\omega}$  are functions of  $\nu$  and n alone. This circumstance makes Nagaoka's system extremely simple; but it must be distinctly noticed that the simplification is only obtained at the expense of neglecting the effect of the negative swarm (3), and therefore applies only to rings which are small compared with the whole system (§ 22).

§ 24. In order to calculate the roots of these equations Nagaoka assumes that  $n/\nu$  is so small that the roots can be expanded in ascending powers of the quantities  $J/\nu$ ,...

Neglecting higher powers he finds, for each value of k, the following frequencies (relative):

Axial vibrations—undamped ( $\kappa = 0$ ).

$$\frac{q_1}{\omega} = 1 - \frac{J - K}{2\nu}, \qquad \frac{q_2}{\omega} = -1 + \frac{J - K}{2\nu}.$$

Orbital vibrations.

Two undamped vibrations ( $\kappa = 0$ ).

$$\frac{q_3}{\omega} = 1 + \frac{4N - L - 2K - 4M}{2\nu}, \quad \frac{q_4}{\omega} = -1 - \frac{4N - L - 2K + 4M}{2\nu}.$$

One damped vibration.

$$\frac{q_5}{\omega} = \frac{2M}{\nu}, \quad \frac{\kappa_5}{\omega} = \sqrt{\frac{3\overline{N}}{\nu}}.$$

One vibration of instability of the same frequency.

$$\frac{q_6}{\omega} = \frac{2M}{\nu}, \quad \frac{\kappa_6}{\omega} = -\sqrt{\frac{3N}{\nu}}.$$

The first four vibrations have relative frequencies very nearly equal to  $\pm \omega$ . It must be noted that a negative frequency is to be interpreted as equivalent to an equal positive frequency. Hence in future negative frequencies will not be specially distinguished from equal positive ones.

§ 25. These vibrations give rise to the following waves.

Axial vibrations—two sets of undamped waves for which the absolute frequencies are given by

$$\frac{N_1}{\omega} = k + 1 - \frac{J - K}{2\nu}, \qquad \frac{N_2}{\omega} = k - 1 + \frac{J - K}{2\nu},$$

where k takes n values between  $\pm \frac{n}{2}$  (§ 15).

These frequencies are not all different. Since J-K is an even function of k, the frequencies  $(N_1)$  for k=-1,-2,... are the same as the frequencies  $(N_2)$  for k=+1,+2,... and vice versa. Further we have  $J_0=0$ ,  $J_1=K$ . Thus omitting all zero frequencies we get finally a set of frequencies given by the scheme

$$\frac{N}{\omega} = \begin{cases}
1 + \frac{K}{2\nu}, & 2, & 3 - \frac{J_2 - K}{2\nu}, \dots \\
1 + \frac{J_2 - K}{2\nu}, \dots & . & .
\end{cases}$$
(15)

Only those frequencies have been written down which can

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correspond to observable spectrum-lines, namely those for k=0,  $\pm 1$ , and exceptionally  $k=\pm 2$ .

Orbital vibrations.

In the same way as above, remembering that N, L are even and M is odd, and that  $N_0$ ,  $L_0 + 2K$ ,  $M_0$  all vanish, we obtain the set of undamped waves

$$\frac{\mathbf{N}}{\boldsymbol{\omega}} = \frac{4\mathbf{N}_{1} - \mathbf{L}_{1} - 2\mathbf{K} + 4\mathbf{M}_{1}}{2\nu}, \begin{cases}
1, \ 2 + \frac{4\mathbf{N}_{1} - \mathbf{L}_{1} - 2\mathbf{K} - 4\mathbf{M}_{1}}{2\nu}, \ 3 + \frac{4\mathbf{N}_{2} - \mathbf{L}_{2} - 2\mathbf{K} - 4\mathbf{M}_{2}}{2\nu}, \dots \\
1, \ 2 - \frac{4\mathbf{N}_{1} - \mathbf{L}_{1} - 2\mathbf{K} - 4\mathbf{M}_{1}}{2\nu}, \ 3 - \frac{4\mathbf{N}_{2} - \mathbf{L}_{2} - 2\mathbf{K} - 4\mathbf{M}_{2}}{2\nu}, \dots \\
1 + \frac{4\mathbf{N}_{2} - \mathbf{L}_{2} - 2\mathbf{K} + 4\mathbf{M}_{2}}{2\nu}, \dots \\
1 - \frac{4\mathbf{N}_{2} - \mathbf{L}_{2} - 2\mathbf{K} + 4\mathbf{M}_{2}}{2\nu}, \dots
\end{cases}$$
(16)

Lastly we obtain a set of damped waves, and a set of waves of instability of the same frequency, given by

$$\frac{N}{\omega} = \begin{cases}
1 + \frac{2M_1}{\nu}, & 2 + \frac{2M_2}{\nu}, \dots \\
1 - \frac{2M_1}{\nu}, & 2 - \frac{2M_2}{\nu}, \dots
\end{cases}$$
(17)

§ 26. Remembering that the suffixes 0, 1 correspond to relatively strong, and 2 to weak lines, we see that a single ring can give rise to the following lines:

(a) A strong line of small frequency  $\omega \frac{4N_1-L_1-2K+4M_1}{2\nu}$ .

(b) An octet of 5 strong lines and 3 very weak lines, all of frequency  $\omega$  very nearly.

(c) A quintet of 3 strong lines and 2 very weak lines, all of frequency 2ω very nearly.

(d) A triplet of 3 very weak lines, of frequency 3 w very nearly.

In general the very weak lines will not be observable. If all the frequencies are such that all the lines fall within the limits of the visible spectrum, we get three strong lines, simple or complex, and occasionally a fourth very weak line.

If Nagaoka's assumption that  $\nu$  is very large compared with n be not true, the results are altered to a certain extent, but not very materially until the quantity K becomes comparable with  $\nu$ ; this requires that n be comparable with  $\nu$ , a contingency which can hardly occur unless  $\nu$  be small.

These results show clearly that a single ring cannot possibly account for spectrum series, and that for two reasons:

(1) The absolute frequencies (N) are approximately in

arithmetical progression.

- (2) The number of lines observable is far too small, because, as I have proved elsewhere, the intensities of successive lines after the first two or three diminish far too rapidly.
- § 27. We must now examine whether a system of ring can account for spectra, each ring contributing one or more lines. This view it is true has difficulties; for the similarity in the structure of lines of the same series, and in their behaviour in a magnetic field and under pressure, is frequently assumed to indicate that they are produced by the same vibrator. But seeing that all rings of the same system are necessarily linked together, perhaps all that we need assume is that they are produced by vibrations of the same type, though of different rings. Thus it becomes necessary to investigate under what conditions the frequencies (N) just found fall within the limits of the spectrum. For this purpose it is necessary to estimate the value of  $\omega$ .

 $\omega$  is given by equation (10) of § 23. Introducing the

quantity  $\beta = \omega \rho / C$ , we get

$$\boldsymbol{\omega} = \frac{m \cdot \mathbf{C}^3 \boldsymbol{\beta}^3}{(\mathbf{v} - \mathbf{K})e^2} \quad . \quad . \quad . \quad . \quad (18)$$

and

$$\rho = \frac{(\nu - \mathbf{K})e^2}{m\mathbf{C}^2\beta^2}.$$
 (19)

We must remember that the table of § 19 gives an upper limit to the value of  $\beta$  for each value of n. Thus when  $n, \nu$  are given, equations (18), (19) give respectively upper and lower limits for  $\omega$ ,  $\rho$ , which must not be transgressed if the

system is to give fine spectrum-lines.

Again, an upper limit for  $\rho$  is given by the condition that the ring must be small compared with the whole system (§ 22); thus  $\rho$  cannot be as large as the radius of the atom which the system represents. With this upper limit for  $\rho$  equation (19) gives a lower limit for  $\beta$ , and equation (18) a lower limit for  $\omega$ , quite independently of the condition for fineness of the spectrum-lines.

This condition, however, with the table of § 19 gives a lower limit  $(n_0)$  for n, This is obvious on hypothesis (A), where n is determined by  $\beta$  by the table. On hypothesis (B) we saw that to produce lines of a given fineness and degree of homogeneity, the value of n given by the table is the least

458 possible for the assigned value of  $\beta$ ; any smaller value would

give broader lines and shorter wave-trains (§ 19).

Since  $\nu$  is the total number of negative electrons in the system, whether all be grouped in rings or not, the quotient  $\nu/n_0$  gives the greatest possible number of rings of the system which can produce lines of the requisite fineness. This number is probably very considerably overestimated, for it assumes that nearly all the rings have the same number of electrons, while it is nearly certain that many of them have many more than the lower limit  $(n_0)$  for n just found. Multiplying  $\nu/n_0$  by the number of lines given by a single ring, we get an upper limit for the number of lines given by the system.

§ 28. In order to see what kind of results can be obtained in this way with different assumptions, we shall make the calculation for the values  $\nu = 10, 100, 1000, 10,000, 100,000$ and for  $\rho = 10^{-9}$ ,  $10^{-8}$ ,  $10^{-7}$  cm. The constants required are  $e^2/mC^2$ , and  $mC^3/e^2$ . For small velocities  $m = 6 \cdot 10^{-28}$  gr.,

 $e = 3.5 \cdot 10^{-10}$  (E.S.U.),  $C = 3 \cdot 10^{10}$  cm. Hence

$$e^2/mC^2 = 2\cdot 2 \cdot 10^{-13}$$
,  $mC^3/e^2 = 1\cdot 4 \cdot 10^{23}$ .

For larger velocities m is greater but a sufficient correction is easily applied.

The method of calculation is best understood from a parti-

cular case, say  $\nu = 1000$ ,  $\rho = 10^{-9}$ .

Neglecting K we get by (19)  $\beta^2 = 0.22$ . Thus to a first

approximation  $\beta = 0.47$ ,  $n_0 = 66$ .

This is too large for us to neglect the change in mass, which amounts to an increase of about 7 per cent. according to Kaufmann. The value of K for  $n_0 = 66$  is about 48, practically 5 per cent. of  $\nu$ . Thus on the whole we must decrease  $\beta^2$  by 12 per cent., and  $\beta$  by 6 per cent., getting  $\beta = 0.44$ ,  $n_0 = 59$ .

The following table gives the results of the calculation.

7'=	10.		100.		1000.		10,000.		100,000.						
ρ	β.	ω.	$n_0$ .	β.	ω.	$n_0$ .	β.	ω.	$n_0$ .	β.	ω.	$n_0$ .	β.	ω.	$n_0$ .
10-9	.036	110	11	·14	400	19	•44	1300	59	>1			>1		
10-8	.013	4.2	8	.046	14	11	.15	44	19	.45	140	61	>1		
10-7	.0043	0.13	6	.014	0.45	3	.047	1.4	11	.15	4.4	19	•46	15	62

The unit for  $\omega$  is  $10^{16}$  revolutions per sec.

The frequency, measured by  $2\pi C/\lambda$ , in the same unit is 1.9 for the extreme ultraviolet, 0.24 for the extreme red, 0.48 for the violet.

§ 29. In studying the frequencies of the lines of the four types given in § 25 we must bear in mind that Nagaoka's expressions presuppose that  $\nu$  is large; for values of  $\nu$  less than 100 they give only rough approximations to the truth. As a matter of fact we are interested mainly in systems for which  $\nu$  is large, on account of the difficulty as to stability; the small values are merely added for the sake of completeness.

Type (a).—
$$N = \omega \frac{4N_1 - L_1 - 2K + 4M_1}{2\nu}$$
.

By § 20 we find

$$4N_1-L_1-2K+4M_1=4.03n\left(Log n-0.300+\frac{0.23}{n^2}\right)$$

where Log denotes the common logarithm.

For 
$$n = 6$$
,  $4N_1 - L_1 - 2K + 4M_1 = 11.7$ .

For 
$$n = 60$$
,  $4N_1 - L_1 - 2K + 4M_1 = 357$ .

For 
$$n = 450$$
  $4N_1 - L_1 - 2K + 4M_1 = 4275$ .

Fif we assume that all the rings in each system have different numbers of electrons, as for instance is the case in J. J. Thomson's model, but that the larger rings differ only by one electron at a time, then the number of electrons in the

largest ring, r, is given by  $\frac{r(r+1)}{2} = \nu$ . The values are, for

$$\nu = 10$$
, 100, 1000, 10,000, 100,000,  $r = 4$ , 14, 44, 141, 447,

where the values for 10, 100 can only be regarded as rough approximations, since for small rings the difference from ring to ring may exceed one unit.

These numbers show that the largest ring in every system gives a line of type (a) in the observable spectrum for some value of  $\rho$  between 10<sup>-8</sup> cm. and 10<sup>-7</sup> cm. Thus every system may give as many lines of this type as it has rings with a number of electrons at least equal to  $n_0$  for the given

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system. Hence the largest possible number of lines of type (a) are, for

$$\nu = 10,$$
 100, 1000, 10,000, 100,000, 1, 7, 34, 123, 386,

on the supposition (1) that the number of electrons is different,

but only by one unit, from ring to ring.

On the very much less likely supposition (2) that the rings all have the same number of electrons, and that the least possible  $(n_0)$ , we get absolutely the largest possible number of lines, namely, for

$$\nu = 10,$$
 100, 1000, 10,000, 100,000, 1, 12, 90, 526, 1612.

§ 30. Type (b).— $N = \omega$  nearly.

The table (§ 28) shows that these lines only fall within the observable spectrum for systems for which  $\nu < 1800$ , for larger systems they lie beyond the extreme ultraviolet.

Type (c).  $-N = 2\omega$  nearly.

These lines fall within the observable spectrum when  $\nu < 470$ , otherwise they lie beyond the ultraviolet.

Type (d).— $N = 3\omega$  nearly.

These lines fall within the observable spectrum when  $\nu < 210$ , otherwise they lie beyond the ultraviolet.

We must also remember that lines of type (d) are very

weak and can only be seen in exceptional circumstances.

§ 31. Collecting our results together, we conclude that the number of lines to be expected is probably less than the value (1), and certainly less than the value (2), given in the following table:—

		ν	=	10,	100,	1000,	10,000,	100,000.
No. of	strong	line	s(1) =	3,	21,	68,	123,	386.
,,	weak	,,	(1) =	1,	7,	0,	0,	0.
,,	strong	,,	(2) =	3,	36,	180,	526,	1612.
,,	$\mathbf{weak}$	29	(2) =	1,	12,	0,	0,	0.

All these are estimated on the assumption that  $10^{-7}$  cm. is the maximum allowable radius, even for the largest rings. A smaller maximum materially reduces the values given; in fact a maximum  $10^{-8}$  cm. gives no lines whatever for any system (§ 29).

§ 32. In order to identify these systems with atoms we must calculate their masses and compare them with the atomic weights, bearing in mind that the mass of the hydrogen atom

is equal to that of 1700 negative electrons.

If M be the mass of the positive charge and A the atomic weight of the atom, we find at once

$$A = \frac{\nu}{1700} + \frac{M}{1700m}, \quad . \quad . \quad . \quad . \quad (20)$$

so that  $1700 \,\mathrm{A}$  is an upper limit to the value of  $\nu$ .

Thus we find that a system, representing the H atom in mass, cannot give more than 92 lines (1), or 130 lines (2), in all.

Similarly, a system representing the Fe atom, for which  $\nu < 95,200$ , cannot give more than 376 lines (1), or 1560 lines (2).

These numbers include all the lines that can be given by the system under all possible conditions, whether they occur in series, or in bands, or as stray lines. When we consider that they are upper limits for the selected values of  $\rho$  and  $\nu$ , while these selected values are themselves in all probability chosen too high, we are driven to the conclusion that a single system, constructed on Nagaoka's model, cannot account for spectra as we know them; but we cannot on these grounds reject the possibility that such a system may account for a part of a spectrum,  $e.\ g.\ a$  band or series, or even for a single spectrum of the element.

To decide this question we must consider the stability of the

system.

§ 33. In § 24 we saw that each of the n sets of orbital vibrations includes a vibration of instability, that is a vibration whose component vibrations in the plane of the orbit  $(\xi, \eta)$ 

are proportional to 
$$e^{\kappa t} \cos \left( qt - k\frac{2\pi i}{n} + \alpha \right)$$
, with  $\kappa = \omega \sqrt{\frac{3N}{\nu}}$ .

The frequency of the emitted wave is  $q = \omega \left(k \pm \frac{2M}{\nu}\right)$ , prac-

tically  $k\omega$ ; its period (T) is  $2\pi/k\omega$ . Hence  $\kappa = \sqrt{\frac{3N}{k^2\nu}} \cdot \frac{1}{T}$ , which means that during each period the amplitude is

which means that during each period the amplitude is multiplied  $e^{\sqrt{3N/k^2\nu}}$  times.

By § 20 we have

$$N/k^2 = 2K \sum_{s=0}^{s=k-1} \frac{(k-s-\frac{1}{2})^2}{k^2} \cot \frac{(2s+1)\pi}{2n},$$

for k>0, zero for k=0. The greatest value of  $N/k^2$  obviously *Phil. Mag.* S. 6. Vol. 15. No. 88. *April* 1908. 2 I

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occurs for k=1, and is equal to  $2K-\frac{1}{4}\cot\frac{\pi}{2n}$ , that is, approximately equal to 0.733.  $n\left(\log n - 0.162 + \frac{0.12}{n^2}\right)$ . Using the minimum values of n given in the table of § 28 we find, for

$$\nu = 10,$$
 100, 1000, 10,000, 100,000,  $\sqrt{\frac{3N}{k^2\nu}} \ge 90.$  38, 15, 07, 05.

The method of reckoning here adopted is the one which is most convenient for our purpose; we compare the increases in amplitude of the waves, not after one revolution of the ring, but after one period of each wave, the period being of course less for the waves with the greater number of loops. With the former method of reckoning the waves with the greatest value of k are the most dangerous, with our present method those for which k=1. The latter is obviously more favourable to the ring than the former.

The physical interpretation of the numbers given is obvious; in a system of 10 electrons an initial disturbance of the type considered is at least doubled in '77 period, in a system of 100,000 electrons in 13.9 periods. In the usual sense we

should say that the ring is unstable.

§ 34. To this conclusion Nagaoka \* raises two objections:

(1) Since the frequency  $\left(\omega \frac{2M}{\nu}\right)$  is small, the vibration in question does not enter into the system in general.

(2) The analysis only holds for small oscillations.

As to the first objection, we must remember that  $\omega \frac{2M}{\nu}$  measures the frequency relative to the ring; the frequency of the corresponding emitted wave is the absolute frequency  $\omega \left(k \pm \frac{2M}{\nu}\right)$ ; the external waves which most strongly excite the dangerous vibration have the same absolute frequency. Any external wave of nearly the same absolute frequency will excite it to a certain extent, the more strongly the more nearly coincidence of frequencies is approached. Now the system emits orbital waves of frequency more or less nearly equal to  $k\omega$  (§ 25), which are in fact assumed by Nagaoka to account for spectrum-lines. Hence when the system is not isolated, but surrounded by a large number of similar systems all emitting these waves, it is necessarily subject

<sup>\*</sup> Nagaoka, Tokyo Proc. vol. ii. No. 17, p. 4.

to waves which are capable of exciting the dangerous vibra-

tions in question to a greater or less extent.

As to the second objection, it is of course a valid one; but it can be surmounted by taking higher powers of the disturbance into account. We shall find that for our purpose it is quite unnecessary to pursue the investigation so far as to decide whether, after a greater or less excursion from the circular shape, the ring returns or does not return to its original condition; that is to say, whether it is stable or not in the usual sense. We can apply the condition of § 5, that the ring must give trains of a minimum number of waves, whose period does not change during emission by more than an assigned small fraction of its value.

§ 35. The equations of motion of an electron of the ring are, for motions in the plane of the orbit, which alone concern

us here,

$$r\left(\frac{d\theta}{dt}\right)^2 - \frac{d^2r}{dt^2} = \frac{P}{m}, \quad . \quad . \quad . \quad (21)$$

$$r\frac{d^2\theta}{dt^2} + 2\frac{dr}{dt}\frac{d\theta}{dt} = \frac{\mathrm{T}}{m}, \quad (22)$$

where P, T are the mechanical forces towards the centre and along the tangent.

When the ring is disturbed we have

$$r = \rho - \eta,$$
  $\theta = \omega t + \xi/\rho,$   
 $\eta = \rho A \epsilon^{\kappa t} \sin(gt + \alpha),$   
 $\xi = \rho B \epsilon^{\kappa t} \cos(gt + \alpha),$ 

where

for free vibrations on the supposition that linear terms only need be taken into account.

For another electron of the ring, the ith from the selected one, we have

$$\theta \!=\! \omega t \!+\! \xi_i \!/ \rho \!+\! \frac{2\pi i}{n}, \quad r \!=\! \rho \!-\! \eta_i,$$

where  $\xi_i$ ,  $\eta_i$  involve  $qt + \alpha - k\frac{2\pi i}{n}$  in place of  $qt + \alpha$ .

The force P involves a term  $\frac{\nu e^2}{(\rho - \eta)^2}$  due to the attraction of the central positive charge, together with a small term due to the electrons of the ring from i=1 to i=n-1; the force Tinvolves the latter term alone. Nagaoka's analysis depends on the fact that the latter terms are small in comparison with the first; we may assume that this remains true, provided the disturbance never becomes very nearly equal to the

distance between neighbouring electrons of the undisturbed ring. Even for values of  $\nu$  as great as 100,000 we saw in § 29 that rings of more than 450 electrons can hardly occur; we must suppose the radius to be comparable with  $10^{-7}$  cm. if they are to give observable spectrum-lines. This makes the distance between neighbouring electrons equal to  $10^{-9}$  cm. at least. Hence the disturbance must be supposed to be appreciably less than this value.

§ 36. On this assumption we may neglect the effect of the squares of the small terms,  $\xi^2$ ,... in the small terms of P, and altogether in T. Taking the averages of the equations of

motion for one period we find

$$\omega^{2}\rho - 2\omega \frac{\overline{\dot{\xi}\eta}}{\rho} + \frac{\overline{\dot{\xi}^{2}}}{\rho} = \frac{\overline{P}}{m}, \quad . \quad . \quad (23)$$

$$\overline{\ddot{\xi}\dot{\eta}} + 2\overline{\dot{\xi}\dot{\eta}} = 0, \quad . \quad . \quad . \quad (24)$$

where the cross-bar denotes average values.

In averaging we may obviously neglect the variation of the factor  $e^{\kappa t}$  during one period, particularly if we suppose t to refer to the middle of that period. Hence

$$\overline{\ddot{\xi}\dot{\eta}} = \overline{\dot{\xi}\dot{\eta}} = 0;$$

so that (24), and therefore (22), is still satisfied. Further

$$\begin{split} \overline{\dot{\xi}\eta} &= -\frac{1}{2}q\rho^2 \mathbf{A} \mathbf{B} \epsilon^{2\kappa t}, \qquad \overline{\dot{\xi}^2} = \frac{1}{2}q^2 \rho^2 \mathbf{B}^2 \epsilon^{2\kappa t}, \\ \overline{\mathbf{P}} &= \frac{q\nu e^2}{2\pi} \int_0^{2\pi/q} \frac{dt}{\rho^2 \{1 - \mathbf{A} e^{\kappa t} \sin{(qt + \alpha)}\}^2} = \frac{\nu e^2}{\rho^2 (1 - \mathbf{A}^2 \epsilon^{2\kappa t})^{\frac{3}{2}}} \end{split}$$

so far as it depends on the central charge.

The part due to the ring is  $-\frac{Ke^2}{\rho^2}$ , as before. Thus the equation (23) becomes

$$\omega^2 \cdot \left(1 + \frac{q}{\omega} AB e^{2\kappa t} + \frac{q^2}{2\omega^2} B^2 e^{2\kappa t} \right) = \frac{\nu e^2}{m\rho^3 (1 - A^2 e^{2\kappa t})^{\frac{3}{2}}} - \frac{Ke^2}{m\rho^3}$$

Now equation (22) gives to a first approximation

$$\frac{\mathbf{B}}{\mathbf{A}} = -\frac{\frac{2q}{\omega} + \frac{\mathbf{M}}{\nu - \mathbf{K}}}{\frac{q^2}{\omega^2} - \frac{\mathbf{N}}{\nu - \mathbf{K}}} \cdot$$

With this value we find that the factor of  $\omega^2$  becomes

$$1 - \frac{2N + M}{2(\nu - K)} AB \epsilon^{2\kappa t}$$

very nearly, the second term of which is very small compared with  $A^2e^{2\kappa t}$ , since  $\frac{2N+M}{2(\nu-K)}$  is small. Hence we get very nearly

$$\omega^{2} = \frac{(\nu - K)e^{2}}{m\rho^{3}(1 - A^{2}\epsilon^{2\kappa t})^{\frac{3}{2}}}, \quad . \quad . \quad . \quad (25)$$

for in the small term  $\frac{\mathrm{K}e^2}{m
ho^3}$  we may without appreciable error

put  $1 - A^2 e^{2\kappa t}$  in place of unity.

Comparing (25) with (10) of § 23, we see that the effect of the second and higher order terms is the same as if the area of the ring underwent a progressive diminution, its value after a time t from the beginning of the disturbance being less by the fraction  $A^2 \epsilon^{2\kappa t}$ . The effect on  $\omega$  is to produce an increase of nearly  $\frac{3}{4}$  of this amount; and since every frequency is proportional to  $\omega$ , the frequency of every line increases by the same fraction of its initial value. This change is obviously not one which can be counteracted by the expansion of the electron on hypothesis (A), because it is a progressive change while the latter is secular.

§ 37. At this stage we introduce the condition of fineness and homogeneity of spectrum-lines (§ 5). In order to be on the safe side let us only assume trains of 100,000 waves, and lines of 1 A.U. width, and let us neglect the part of the width due to Doppler effect. In other words, we assume that the frequency of the lines does not change by more than one ten thousandth of its value during one hundred thousand

periods. Is this consistent with equation (25)?

By § 33 the value of  $\kappa$  is  $\sqrt{\frac{3N}{k^2\nu}}\frac{1}{T}$ , which for a system of

1000 electrons is at least equal to  $\frac{0.15}{T}$ . Hence for  $t = 10^5$ . Twe find  $\frac{3}{4}A^2e^{2\kappa t} > \frac{3}{4}A^2 \cdot e^{3\cdot 104} > A^2 \cdot 10^{13000}$ .

This must not exceed 10<sup>-4</sup>. Hence we find

$$A < 10^{-6500}$$
.

Obviously the value of A is not appreciably affected by the fineness of the lines, but only by the value of  $\kappa$ , and especially

by the number of waves in a train. If this be supposed to be only ten thousand in place of one hundred thousand, the limit for A is increased to  $10^{-650}$ .

§ 38. By the ordinary theory of resonance we know that a periodic disturbing force excites every free vibration of the system on which it acts to a greater or less extent, unless it be localized at the nodes of one of the free vibrations, which in that case is not excited at all. But the waves which act on our system are not so localized, and necessarily excite the vibrations of instability as well as all the others; so that amplitudes greater than  $10^{-6500}$ , or for that matter greater than  $10^{-650}$ , are certain to occur. It follows that Nagaoka's model cannot give trains of as many as 105 or even 104 waves; and that interference phenomena with large phase differences are impossible for the waves emitted by it. Hence it cannot account for optical phenomena by means of its free vibrations, quite apart from the difficulty of accounting for fine spectrum- lines in sufficient number. Nevertheless its study is extremely instructive, for on account of its simple structure it is possible to obtain numerical results and deduce definite conclusions. Besides, the interesting properties studied by Nagaoka in his later papers for the most part are not due to his particular assumption of a central positive charge, but to the arrangement of the negative electrons in rings, and so may be expected to belong to other ring systems

It should be particularly noted that the arguments of §§ 33–37 apply to all systems possessing frequency equations with complex roots. We may therefore conclude that in general no system can account for long wave-trains unless the imaginary part of each of its frequencies is vanishingly small (of order  $10^{-5}$  or so) in comparison with the real part.

§ 39. It will be convenient here to summarize the conclusions to which we have been led during the course of this

investigation.

In the first place, we have been led to assign new meanings to the terms "permanence" and "stability." No system which includes electric charges in orbital motion can be absolutely permanent, for orbital motions always imply radiation of energy. By the introduction of the hypothesis of an expanding electron we can, it is true, supply the loss of energy at the expense of the intrinsic energy of the electrons, and so give the system, as it were, a permanence of a higher order, which we may call secular; but obviously sooner or later the structure of the system must be changed. Therefore

we call a system "permanent" when it lasts sufficiently long to satisfy the observed conditions as to constancy of mass and

of other properties.

Such a system may be stable or not in the ordinary sense; that is to say when disturbed in any way, the disturbance may diminish and the system come back to its original configuration, except in so far as that configuration has been altered by radiation; or the disturbance may increase until the system falls away altogether from that configuration. Whichever happens, we call the system "stable," when the progressive change in it, produced by terms of the second order in the disturbance, is so slow as to permit of the emission of trains of many waves and of the production of spectrum-

lines of the fineness actually observed.

When the structure of the undisturbed system is fixed by the hypothesis (A) of the expanding electron, its free periods of vibration are determinate, although subject to secular changes. If it be stable it can produce fine spectrum-lines when disturbed, and the observed width of the lines must be accounted for by means of secondary causes, Doppler effect and the like. But if the hypothesis (A) be not adopted, then a part of the width must be ascribed to progressive changes of period due to unbalanced radiation. We have seen that in any case a degree of permanence sufficient to allow of the production of fine spectrum-lines can only be expected from systems built up of coaxal circular rings of equidistant electrons, because other systems involve radiation, on account of mutual perturbations of their electrons, which cannot be balanced by the energy set free by the expansion of these electrons.

As regards the particular model of Nagaoka, we have seen that it can give a large number of spectrum-lines, but not sufficient to account for a whole spectrum by means of the free vibrations of a single system, however numerous its electrons may be. Further, this model is far too unstable to permit of the production of trains of waves long enough to account for the observed phenomena of interference with great path differences.

Physical Institute, Bonn, April 29th, 1907.

XLIV. The Tores of Saturn. By Percival Lowell\*.

N June 19th (1907) a new phenomenon disclosed itself in the Saturnian ring-system. On the morning of that day, the planet being so placed at the time as to present its rings almost edgewise to the earth, a curious detail was observed at Flagstaff in the shadow which then banded the planet's equator. This equatorial shading, which was in truth the shadow of the rings upon the ball, seemed almost to belie its function because of the lack of density it offered to the eye. Far from being dark, it was only moderately dusky, and furthermore presented when first looked at a tripartite appearance. On more careful scrutiny, its lack of homogeneity proved to be due to a narrow black line that threaded it medially throughout its length, the black core being perhaps one-fourth as wide as the less dense background upon which it stood. At the same time the rings themselves could with attention be made out as the finest knife-edge of light cutting the blue of space on either side the planet's disk. As the sun was at that moment 32' north of the plane of the ringsystem, while the earth was 2° 16′ south of it, the two were on opposite sides of the system, which fact combined with its then visibility shows that the rings are never wholly lost in the Flagstaff glass.

The planet was not looked at again at Flagstaff until October 31, other work occupying the observatory in the meantime. In November, however, it was critically studied. The dusky band was evident as in June and the black line made core to it as before, being plainly perceptible to all the observers. On the 12th and 13th of the month I measured both with the micrometer, the measures on the latter date being the more numerous and exact; for the band was then measured between the threads, outside them and from centre to centre of the same, while the thread-like core was estimated in terms of the thread itself. The mean of the measures with the suitable corrections applied gave;—

for the whole shadow ......  $0''\cdot 46$  and for its black core .....  $0''\cdot 10$ 

The band was tinged a faint cherry-red (Nov. 5); rather more strongly so than the planet's own belts which could be seen both north and south of it. The black medial line in the midst of it was by no means even. It both undulated slightly and showed irregularities of outline, one black bead

<sup>\*</sup> Communicated by the Author.

in especial being noticeable about halfway from the planet's centre to its (the planet's) eastern limb (Nov. 13, 14<sup>h</sup> G.M.T.). The line also seemed not quite central in the belt but a little nearer its northern edge. The sun was now 1° 39′·5 south of the ring-plane, while the earth was 50′ north of it. So that both bodies were now again on opposite sides of it, having respectively changed across.

Although seen by all the observers at Flagstaff, the black core was not caught by Barnard at Yerkes, nor has it been reported from the Lick. This, however, is in keeping with the definition at the first place disclosed already by its greater

space penetration for stars.

The rings themselves were equally visible, in fact were now easy objects, although, as before, only the edge of their plane was presented to the eye. But, in addition to the general line of their light, agglomerations were plainly discernible on them, attention being directed to that end. The agglomerations were symmetrically placed, two on either side the ball, and continued observation showed them to be permanent in position. Micrometric measures were made upon them by both Mr. Lampland and by me from November 3rd to November 9th. The most complete were those of the latter date, which, while agreeing in place with the earlier ones, gave not only the centre of the agglomerations but their beginning and end in distances from the planet. My measures on that evening, with which those of Mr. Lampland substantially agree, were as follows:—

November	9.	1907.	15 <sup>h</sup>	25m	to	$15^{\rm h}$	50 <sup>m</sup>	G.M.T.

Right. Mean of		In seconds of arc from the nearer limb.	In equat. radii of Saturn from the Planet's centre.
3 measures.	Inner edge of inner thickening	1''.00	1.11
2 ,,	Outer " " "	3".94	1.43
2 ,,	Gap (most conspicuously vacan spot).	nt 5"·36	1.58
3 ,,	Inner edge of outer thickening	6".92	1.75
4 ,, LEFT.	Outer " " "	8".51	1.92
2 measures.	Inner edge of inner thickening	1''.15	1.12
2 ,,	Outer ,, ,,	4".22	1.46
2 ,, 5 ,,	Gap (most conspicuously vacan spot).	t 5"•58	1.60
3 ,,	Inner edge of outer thickening	6".53	1.71
2 ,,	Outer ,, ,, ,,	8".46	1.91

At the sam	ne time measures of the whole ring gav	e:
Mean of		
2 measures.	On the right measured from the nearest	
	limb, reduced to equat. radii from the planet's centre	2.164
1 measure.	On the left measured from the nearest	
	limb, reduced to equat. radii from	
	the planet's centre	2.145
4 measures.	From W. to E. end visible double	

measures, reduced as above

2.191

The equatorial radius, also measured, came out:—Mean of

2 measures . . . . . . . . . . . 9" · 245

Several things are deducible from these measures. First: It is evident that the rings could not be followed quite to the outer limit of ring A, as that stretches to 2.25 or 2.30 radii from the centre of the planet, according to whose measures of the system we adopt, while the measured breadth was now at most 2.19. This implies that the outer part of ring A has less thickness than the rest; for we cannot refer the effect to less breadth of ring there being intersected by the line of sight, since the earth was on the opposite side of the ring-system from the sun. The average width of the thread of light upon which the agglomerations were strung was by comparison with the black core of the shadow not over 80 miles.

Secondly: The present measures indicate that the rings approach the body of the planet closer than they have been measured before.

Thirdly: The measures of the positions of the agglomerations show that Olbers' explanation of them, endorsed by Seeliger, fails to account for the appearances.

Fourthly: These positions point to another explanation of some interest. And

Fifthly: This latter explanation proves also to account for the phenomena of the shadow, and incidentally to answer a query propounded by Seeliger on previous observations of it. To make this clear we will begin by quoting Seeliger upon the observations and deductions on the last occasion when the rings were presented as now edgewise to the earth.

"The ring, according to Mr. Barnard, was completely invisible at the end of October, 1891, even in the most powerful glass of the Lick Observatory. He caught it for the first time on October 30, 1891, 1<sup>h</sup> 7<sup>m</sup> G.M.T. As Mr. Oudemans could see nothing of the ring on October 29, 17<sup>h</sup> 9<sup>m</sup> G.M.T.,

its reappearance falls within the narrow interval between these two dates. At that time the earth had an elevation above the ring of 1° 56'. Mr. Oudemans further remarked on the same day: 'a fine dark streak \* runs across the equator,' and explained this as the projection of the dark ring upon Saturn's disk, because it still remained visible after the Sun had risen a little over the plane of the ring. Against this interpretation there is practically nothing to be said; only it may perhaps be remarked that here might well be the work of the bright ring too. For the shadow made by this ring does not lie exactly between two planes, and a part of it could constantly be found in the shadow of the other ring, even after the Sun had risen a little over the plane of the ring-system. One has thus the advantage of explaining a somewhat greater breadth of the dark streak; and this is to welcomed, as the minor part of the crape ring, as above remarked, is almost completely transparent, and therefore lets the disk of Saturn behind it be seen and itself does not appear quite black."

"Before the ring begins to be visible, it must disclose itself as a dark stripe across Saturn's disk. This was a fact seen and drawn by Mr. Barnard. He found on October 22, for the breadth of the dark band 0".51 and for the position of its middle point from the north limb (of the planet) 7".40; from the south one  $6^{\prime\prime}$ . 56. Mr. Barnard asserts that the measured breadth entirely agrees with the ephemeris data. I find, however, for an elevation of 1° 41' for the earth above the plane of the ring, its width to be 0".16 or 0".24, according as the bright ring alone is considered or the dark ring is included as well. On the contrary, I find very good agreement between the observations and the data for the position of the dark band of 7".64 and 6".72 from the north and south limits respectively, and of 7".60 and 6".76 if the dark ring be also comprised. The above remarked divergence between observation and theory demands explanation, since Mr. Barnard on October 29 found an even greater breadth of the dark band of 0".65."

"From the very interesting notices of Mr. Barnard on the appearance of the ring when it became visible on October 29, 1891 (October 30, 1891?, see above), the following points deserve prominence. The ring could first be seen at a distance of about 2" from the edge of the disk; also the two halves on either side were not the same; and lastly Mr. Barnard

<sup>\*</sup> Mr. Oudemans here refers to the whole shadow, as appears from Barnard's measures of it cited below. Neither he nor Barnard saw its black core.

perceived two bright knots on the western one. The first fact can, if one pleases, be explained by the proximity of Saturn's bright disk; but another circumstance comes in here, as will be shown. The second fact demands no further discussion; while for the explanation of the third Mr. Barnard assumes that he saw two of the inner satellites. But Mimas only could be in question; and it might raise difficulties to explain both knots by it. So the explanation needs no extended discussion, as it appears to me very probable that here another phenomenon is exhibited."

Seeliger then goes on to attribute it to greater showing in the line of sight; and he deduces from the known dimensions of the ring-system the places where such ansal broadening

would cause apparent maxima, to wit:

at 1.60 and 1.98 radii of Saturn from the planet's centre.

We may here remark parenthetically that apparent agglomerations or thickenings of the rings have been noticed by several observers since the time of Herschel, by Bond, Wray and Struve in especial, and agreeing more nearly than the above with the phenomena observed at Flagstaff; but all the observers attributed them to causes other than what we shall now set forth.

Taking up first the shadow phenomena seen at Flagstaff, calculation shows that the shadow of the whole ring-system including the crape ring, with the Sun as on November 9 (1907) 1° 39′·5 above the ring-plane, would be 0″·26 wide only. The position of the Earth does not sensibly change this. Now the shadow was nearly twice as wide as this, being 0″·46. Such then cannot be the cause. Nor can it be the penumbra of the dark core, as that would be but 0″·05 in width, a quantity indistinguishable in fact by the eye. The only explanation left is that in the black core we are looking at the shadow of ring A, practically plane and in the dusky shadow about it through particles situated above and below that plane lying in the other rings. In other words, that ring B and ring C are for the most part not flat rings but tores.

Turning now to the phenomena of the rings themselves, the agglomerations on the Olbers-Seeliger theory of their showing should, as computed in the same memoir by Seeliger, be found at

1.60 and 1.98 radii of Saturn from the planet's centre; for these are the points where the line of sight from the Earth traverses the greatest ansal breadth of the rings at their densest.

Instead, however, of being so found, the present thickenings occur in striking contrast to this, the maxima showing where the minima should and the minima where the maxima would be; since their centres are situate at 1.27 and 1.83 with a conspicuous gap at 1.60 and another falling-off at 1.92 outward. It is not, then, to line of sight massing from

particles in one plane that the observed effect is due.

But the moment we let our thought wander out of the plane we light upon an explanation which satisfies the phenomena. For suppose portions of the rings to be not flat rings but tores, that is, rings after the manner of anchorrings, encircling the planet. Then, viewed edgewise, such a tore would make its presence perceptible by humps of light in two patches symmetrically placed on either side the planet; to wit, at its ansae where the sight-line would penetrate the greatest amount of it. The agglomerations, then, can represent tores, but cannot represent flat rings \*.

Thus we are led by the phenomena presented by the rings to the same explanation to which those of the shadow conducted us. Furthermore, it is to be remarked that the line

\* Note.—It seems necessary to suppose that we see through the ring to its partially illuminated side; for from observations made or published since this article was written, it appears that the agglomerations disappear when either the Sun or the Earth passes through the plane of the rings.

Thus Mr. Lampland's observations of the rings gave:

Dec. 31. Agglomerations visible.

Jan. 1. Ansae too faint to detect structure.

,, 3 & 4. Ansae continuous.

,, 7. No agglomerations. Rings easily seen..

Earlier observations by Aitken at the Lick, July 23—Oct. 12, show that no agglomerations were seen between those dates. See Barnard to the same effect.

Since this was written Barnard has published his observations with his explanations. His explanations, however,—for he gives two—one that the eye sees through the underside of the rings and that such light is greatest where the rings are densest, the other the exact opposite, that the light is most where the ring is least crowded,—are self-condemning on several counts; one, for instance, that the inner condensation does not fall by his own showing on the ansal position of any part of ring A but wholly on the crape ring. Each explanation might possibly account for one agglomeration alone, but for that very reason fails for both together. The presence of the gaps is another fatal objection to them.

As seen at Flagstaff, under the same seeing that disclosed the dark core to the rings' dusky shadow, the agglomerations were fairly continuous, though uneven, for the whole length of them measured on November 9th. Their vertical width was about 0"20, while that of the continuous ring was about 0"02, giving for the width of the main plane

of the rings some 80 miles or 130 kilometres.-P. L.

of argument in each case is independent of the other. For in the one case, in the shadow, we are reasoning on what we note from a transverse viewing of the tores; in the other, the rings themselves, from a longitudinal aspect of them in the bright agglomerations. As the two deductions lead to the same result, each gains corroboration from the other.

So much for the facts. They conduct us to a conclusion of interest from the point of view of celestial mechanics. see this we will briefly recapitulate what has previously been shown of the stability of the rings. Laplace first showed that the rings could not be, as they appear, wide solid rings, inasmuch as the strains due to the differing attraction of Saturn for the several parts must disrupt them. Peirce then proved that even a series of very narrow solid rings could not subsist, and that the rings must be fluid. Finally. Clerk-Maxwell demonstrated that even this was not enough, and that the rings to be stable must be made up of discrete particles, a swarm of meteorites, in fact. But, if my memory serves me right, Clerk-Maxwell himself pointed out that even such a system could not eternally endure, but was bound eventually to be forced both out and in, a part falling upon the surface of the planet, a part going to form a satellite farther away.

Even before Clerk-Maxwell's time, Edward Roche in 1848 had shown that the rings must be composed of discrete particles,—mere dust and ashes. He drew this conclusion from his investigations on the minimum distance at which a fluid satellite could revolve around its primary without being

disrupted by tidal strains.

The dissolution which Clerk-Maxwell foresaw can easily be proved to be inevitable if the particles composing the swarm are not at considerable distances from one another; and that they are not at such distances apart is certainly the case with rings A and B, as is witnessed by the light those rings send us, even allowing for the comminuted form of their constituents. Now a swarm of particles thus revolving round a primary are in stable equilibrium only in the absence of collisions. But in a crowded company collisions, due either to the mutual pulls of the particles or to the perturbations of the satellites, must occur. At each collision, although the moment of momentum of the two particles remains the same, energy is lost unless the bodies be perfectly elastic, a condition not found in nature, the lost energy being converted into heat. In consequence, some particles will be forced in toward the planet while others are driven

out; the greater number falling in until at last they are

brought down upon the body of the planet.

Now the interest of the observations at Flagstaff consists in their showing us this disintegration of the rings in process of taking place, and furthermore in a way that brings before us an interesting case of celestial mechanics.

In considering the action of one body upon another revolving around a third, the points germane to our present inquiry are the perturbations in the radius vector and in the longitude

of the second body.

Now, by the method of variation of parameters the radius vector of the perturbed body—the disturbed particle in the present case—may be expressed, as has been done by Airy, by

$$r_1 = \frac{a_1(1 - e_1^2)}{1 + e_1 \cos(\theta_1 - \omega_1)},$$

where the subscripts refer to the variable elements. The perturbed longitude may similarly be expressed by

$$\theta_1 = n_1 t + e_1 + \left(2e_1 - \frac{e_1^3}{4} + &c.\right) \sin(n_1 t + e_1 - \omega_1) + &c.$$

These may be expanded in an ascending series of terms according to powers of the excentricities and of cosines of multiple arcs of the mean motions of perturber and perturbed by Fourier's series. The resulting expression is composed of terms similar to those in the undisturbed orbit, and of others denoting the effect of the perturbation. The latter are of the typical form:

$$\frac{\mathrm{P}e^{x}e^{\prime x'}}{pn-qn'}\cos\overline{(pn-qn')t-\mathrm{Q}},$$

where P is a function of a and a', the radii vectores of the perturber and perturbed, and of  $\mu$  the mass of Saturn and

the perturbed body.

The form of these terms shows that they will become considerable in proportion as pn-qn' is small, since their coefficients are divided by this quantity. Now as n and n' are the mean motions of perturber and perturbed, if these are commensurate there will always be terms of the sort

which will be large, namely, those in which  $\frac{q}{p} = \frac{n'}{n}$ ; for p and q are always integers, in consequence of the method of expansion.

The various terms with the argument (pn-qn')t will have coefficients of different powers of the excentricities. The lowest of these which can occur in the expressions will be of the order p-q. The term, therefore, in which  $x+x_1=p-q$  is the term least diminished by the excentricity coefficient, and therefore the most potent in its effect.

From this it is evident that two bodies will mutually disturb each other in their revolutions about a third according as

their periods are:

1st. Commensurate.2nd. Differ by the smallest integer.

The most disturbing ratio is when the periods are:—

1:2; 2:3, &c.; the next, 1:3; 3:5, &c.; then, 1:4; 2:5, &c.; and so on.

The initial ratio in each line will be the most effective in that line, because the cycle of the disturbance will be repeated in the time it takes the outer body to come again into conjunction with the inner, and this for the ratio 3:5, for instance, will be three times as long as for that of 1:3.

The same thing can be seen geometrically by considering that the two bodies have their greatest perturbing effect on one another when in conjunction, and that if the periods of the two be commensurate, they will come to conjunction over and over again in the same points of the orbit, and thus the disturbance produced by one on the other be cumulative. If the periods are not commensurate the conjunctions will take place in ever shifting positions, and a certain compensation be effected in the outstanding results. In proportion as the ratio of periods is simple will the perturbations be potent. Thus with the ratio  $1:\overline{2}$  the two bodies will approach closest only at one spot, and always there, until the perturbations thus induced themselves destroy the commensurability of period. With 1:3 they will approach at two different spots recurrently; with 1:4 at three, and so on. The number of points round the orbit at which they will meet is in fact as the sum of the powers of the excentricities in the lowest coefficient of the terms with the commensurable argument.

We see, then, that perturbations, which in this case will result in collisions, must be greatest on the particles having periods commensurate with those of the satellites. But inasmuch as there are many particles in any cross-section of the ring, there must be a component of motion in any collision tending to throw the colliding particles out of the plane of the ring, either above or below it. Such extra-plane particles would, therefore, be most numerous just inside the points of commensurability, because, though the moment of momentum is preserved and thus particles be thrown outward from the point as well as in, owing to the loss of energy they must be more numerous on the inside.

Considering, now, the commensurate ratios between the periods of particle and satellite which can enter into the problem, we find these in the order of their potency to be:

With Mimas, 1:2, 1:3, 1:4, With Enceladus, 1:3, With Tethys, 1:4.

Such periods of commensurability as 2:3 of Mimas and 1:2, 2:3 of Enceladus do not come into question as they take place outside the ring-system. Now calculation shows that the distances corresponding to a period of 1:2 of Mimas, of 1:3 of Enceladus, and of 1:4 of Tethys fall in Cassini's division, which separates ring A from ring B. The first or outer tore should therefore occur just inside that division or in the outer part of ring B. This is precisely where we find it; for the inner edge of Cassini's division is at 1.92 radii of Saturn from the centre of the planet, and the outer tore begins at 1.92, thence to stretch inward toward the disk. Pursuing our inquiry with the next most effective ratio, that of 1:3 of Mimas' period, we note that its corresponding distance falls at the boundary of ring B and ring C at 1.495 radii of Saturn from the centre. Now it is inside this, to wit, at 1.46 and 1.42, that the inner tore begins. Furthermore, this tore is much longer than the outer one. We turn, therefore. to the next most potent ratio, that of 1:4 of Mimas' period, to find that its distance falls at 1.24. This then accounts for the greater length of the inner tore.

The remarkable way in which theory thus accounts for observation is of interest, and the more so from involving a

case of celestial mechanics interesting in itself.

XLV. On the Contact Potential Differences determined by means of Null Solutions. By S. W. J. SMITH, M.A., and H. Moss, B.Sc., Royal College of Science, London \*.

1. Introduction.

4. Palmaer's "null solutions."

7. A method of search for other null solutions.

9. Null solution of KCN.

12. Effect of Na<sub>2</sub>S upon the p.d. between Hg and KCl.

16. Null solution of KCl.

17. Effect of oxygen upon Paschen's relation.

18. Inferences from results obtained with null solutions of KCN and of KCl.

§ 19. Null solution of KI. § 20. Null solution of KO 20. Null solution of KOH. \$ 21. Summary of conclusions.

§ 1. TNTRODUCTION.—The processes which occur during the polarization of electrodes are of considerable theoretical and practical importance. Being largely surface effects, they can be followed, in the case of mercury, by observation of the changes of the surface-tension which result from polarization. Mercury electrodes have been the subject of much study in this way, but while the interpretation of some of the results seems clear, there are others which have been the subject of frequent discussion. Chief amongst these is the significance of the maximum surface-tension between mercury and the electrolyte which occurs at some particular degree of polarization in almost every solution that has been examined. The maximum was for long supposed to indicate zero potential-difference between the mercury and the solution; but the adequacy of this hypothesis, as a general interpretation of the significance of the maximum, is now very doubtful.

§ 2. Evidence was given by one of us (Phil. Trans. A. 1899, pp. 47-87), in discussing the validity of the Lippmann-Helmholtz theory of electrocapillarity, that the maximum surface-tension between mercury and certain electrolytes is not reached when the potential-difference is zero. It was shown that, for equally concentrated solutions of the particular electrolytes KCl and KI, the potential-differences at the respective maxima differ to such an extent that if one is assumed to be zero the other must be nearly a quarter of a volt (l. c. pp. 70, 71). The assumption of zero potentialdifference in either case is arbitrary. It is possible that the potential-difference at the maximum surface-tension is zero in some electrolytes; but the evidence from the electro-

<sup>\*</sup> Communicated by the Physical Society: read February 28, 1908.

capillary curves (l. c. pp. 68 & 82), while not conclusive, favours the view that it is not so in any of the moderately dilute solutions of KCl and KI (giving "depressed" maxima) referred to above.

Palmaer has, however, published experiments recently from which it would seem that in the case of n/10 KCl, the potential-difference at the maximum surface-tension is, if not zero, at least very small. This result, if conclusive, would be of great theoretical value, and we have therefore performed the experiments described below to test the

validity of Palmaer's deductions.

§ 3. Palmaer published in 1903 (Zeitsch. f. Elektrochemie, ix. pp. 754-757) a summary of certain experiments with drop electrodes, by means of which he sought to show that the true contact potential-difference between mercury and n/10 KCl solution is about 0.57 volt, and he has quite recently (Zeitsch. f. physik. Chemie, lix. pp. 129-191, 1907) given a full account of these experiments and of others, from which his final conclusion is that the potential-difference in question is 0.5732 + .0003 volt at 18° C.

One of us found that the maximum surface-tension between mercury and n/10 KCl solution was produced by a polarizing electromotive force of  $0.568 \pm .01$  volt ( $l.\ c.\ p.\ 71$ ). It would thus appear that, after all, in the case of n/10 KCl, the potential-difference at the maximum surface-tension is practically zero, for it is represented by the difference between the two numbers just given. We shall attempt to show however that, although of much interest in connexion with electrocapillarity, Palmaer's deduction from his experiments is not necessarily true, and that his results leave the knowledge of the contact potential-difference between Hg and n/10 KCl substantially in the same state of uncertainty as before.

§ 4. Palmaer's Null Solutions.—When certain conditions, first fully discussed by Paschen, are fulfilled, a mercury electrode immersed in n/10 KCl shows a potential about 0.57 volt higher than that of an electrode of mercury streaming into the same solution. Palmaer found that by adding certain substances to this n/10 KCl solution, he could not only reduce the observed potential-difference between the still and dropping mercury until it became very small, but could cause it, passing through the value zero, to change in sign. In this way he found two different "null solutions," one containing small quantities of KCN, KOH, and  $Hg(CN)_2$ , and

the other H<sub>2</sub>S and a small quantity of acetic acid, for which the potential-difference between the still and dropping electrodes was zero. It is of course well known that a concentrated solution of a mercury salt behaves like a Palmaer null solution in the respect that there is practically no p.d. between still and dropping mercury electrodes immersed in it; but small variations in the composition do not here produce effects of the kind observed by Palmaer. the absence of a p.d. in this case has been explained in a way which is not applicable when the amount of dissolved mercury is very small.

§ 5. Experiments of the kind performed by Palmaer were suggested by Nernst (Ann. d. Physik, lviii. p. 11, 1896), and it is obvious that the results can be explained, either according to the Helmholtz theory of dropping-electrodes or to that of Nernst, if we assume that when the observed E.M.F. is zero a solution has been found which exhibits no potentialdifference with respect to mercury. In such a case there would be no tendency to produce an E.M.F., whether, in the general case, the double-layer potential is altered by extension of the mercury surface (Helmholtz), or whether the doublelayer forms practically instantaneously but is accompanied by concentration changes in the solution (Nernst).

§ 6. Connecting each of his null solutions in turn to a solution of n/10 KCl, Palmaer measured the p.d. between mercury in the null solution and mercury in the n/10 KCl. Allowing for small contact potential-differences between the electrolytes, he found practically identical values (of which the mean is the number already quoted) for the p.d. Hg | n/10 KCl. Strictly, these measurements prove only that the p.d. between mercury and each of the null solutions

was the same.

Palmaer found only two satisfactory null solutions; but experiments with several others are described below. From these experiments it will be seen that the p.d. between mercury and a null solution of the type described by Palmaer is not always the same, and hence is never necessarily zero as Palmaer assumes.

§ 7. A method of search for other Null Solutions.—In searching for other null solutions we were guided by the relation deducible from Paschen's experiments, that although the p.d. between Hg and an electrolyte when the surfacetension is a maximum need not be zero, it is nevertheless always equal to the p.d. between a dropping electrode of the

Paschen type (Wied. Ann. xli. p. 42, 1890) and the same electrolyte (cf. Phil. Trans. l. c. pp. 83 et seq.). We have found, in the course of the present experiments, that the statement of this relation, which is one of the most important in electrocapillarity, requires qualification. The relation is true only when the medium through which the mercury falls before it enters the solution does not contain a constituent which interacts chemically with the mercury and the solution. In some cases, for example, the relation does not hold until the air surrounding the dropping electrode and the solution is replaced by hydrogen, nitrogen, or other non-oxidising medium.

§ 8. Assuming the truth of the above relation, it was obvious that any solution for which the maximum of the electrocapillary curve lay at the origin (applied E.M.F. zero) would be a null solution. If the maximum for a given solution were slightly (a) to the right or (b) to the left of the origin, then the still electrode for that solution would be slightly (a) positive or (b) negative to the dropping electrode. The change in sign of the potential of the dropper with respect to the still electrode, with a small change in the composition of the electrolyte, would not correspond necessarily (as assumed by Palmaer) with a change in the sign of the potential of the still mercury with respect to the solution, but only with a change from one side of the origin to the other of the maximum of the electrocapillary curve.

Since it is almost certain that this maximum does not always correspond with zero potential-difference, it seemed equally certain that a null solution of the kind studied by Palmaer could not always, and need not ever, be one

exhibiting no contact p.d. with respect to mercury.

§ 9. Null Solution of KCN.—It has long been known that moderately concentrated solutions of KCN give electrocapillary curves of which the maxima lie to the left of the origin (applied E.M.F. negative), while weaker solutions give curves of which the maxima lie to the right. If a solution could be found of which the maximum lay at the origin, this would be a null solution of the kind studied by Palmaer. A null solution of KCN was apparently found approximately by Amelung in a research which Palmaer describes (Zeits. f. physik. Chemie, lix. p. 164, 1907) but regards as unsatisfactory. This solution used according to Palmaer's method would give a value of roughly 0.7 volt for the contact potential Hg | n/10 KCl. It was obtained by

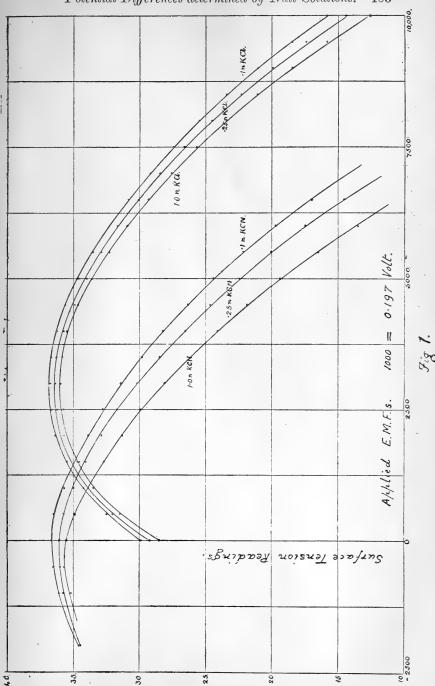
gradual dilution of a saturated solution of KCN until the p.d. between the drop electrode and the still electrode became zero.

We have found and examined a null KCN solution in another way. A normal solution of KCN was made up and this, together with weaker solutions of definite strength, obtained from it by dilution, was then examined as described below. As it was found that the electrocapillary properties of solutions, apparently of equal concentration, produced from different samples of KCN frequently differed considerably, the precise constitutions of the different solutions cannot be specified. This, however, is of no importance to the validity of the experiments. For the sample of KCN used in the experiments, the null solution contained about 0.26 n KCN; but another sample from another source would probably have given a different result.

The following quantities were observed in the case of each solution:—

- 1. The electrocapillary curve—the reading for maximum surface-tension, and the E.M.F. required to produce it, being noted as carefully as possible.
- 2. The electrocapillary curve of a solution of KCl of equal strength.
- 3. The horizontal distance between the descending branches of the two curves (cf. Phil. Trans. l. c. p. 69).
  - 4. The E.M.F. of the cell Hg | KCN | KCl | Hg.
- 5. The E.M.F. of the dropping electrode circuit Hg | KCN | Hg, the measurements being taken when the end of the continuous part of the jet was in the surface of the solution (Paschen).
- 6. The E.M.F. of the dropping electrode circuit Hg | KCN | KCl | Hg.

Some of the electrocapillary curves are shown in fig. 1, the others being omitted to avoid confusion. The KCN curves are very flat near the maxima, and the E.M.F.s corresponding to these maxima are relatively difficult to determine.



The chief results of the measurements are summarized in the following Table:—

	1.	2.	3.	4.	5.	6.	7.
Strengths of solutions.	KCN (scale-	KCl (scale-	E.M.F. of Max. S.T. KCN	Horizontal distance between curves.	KCN KCl +	KCN +	KCN KOI +
borderons.	reading).	reading).	volt.	volt.	volt.	volt.	volt.
0·1 n.	36.65	36.75	.039	645	642	.043	·679
·2 n.	36.30	36.70	·020	·667	·671	.018	·694
·24 n.	36.10	36:53	·010	687	-687	·012	698
·25 n.	36.08	36.35	0	·691	.690	.003	·699
·26 n.	36.04	36.30	0	.696	·693	001	·697
·27 n.	36.00	. 36.27	005	·697	.696	<b>-</b> ·005	.693
·50 n.	35.81	36.17	020	·716	·715	<b>−</b> ·016	·703
1.0 n.	35.70	36.10	059	·748	·745	<b>-</b> ·046	·705

Solutions of KCN and KCl of equal strength being of approximately the same conductivity and degree of ionization (cf. Kohlrausch & Holborn, Leitvermögen der Elektrolyte, pp. 145 & 148), the contact potential-difference between them will be very small, probably less than a millivolt. This is confirmed by the agreement between the numbers in Columns 4 and 5, since the former represents the difference between Hg | KCl and Hg | KCN (cf. Phil. Trans. l. c. pp. 69 et seq.).

Each number in Column 7 should be equal to the sum of the corresponding numbers in Columns 5 and 6. A comparison serves to indicate the limits of the uncertainty of the dropping-electrode measurements. The jet fell freely in contact with the air. By comparison of the numbers in Columns 3 and 6 it will be seen that Paschen's relation held, within the limits of errors of experiment, in every case.

The null solution was that for which the surface-tension was a maximum in the natural state (applied E.M.F. zero). Its strength was, in round numbers, n/4 KCN, and assuming with Palmaer that, in consequence, Hg | n/4 KCN=0, it would give, by Column 5, Hg | n/4 KCl=0.69 approximately.

§ 10. As will be seen later, a solution of n/4 KCl, examined according to either of the methods described by Palmaer, would have given a null solution from which he would have deduced the value Hg | n/4 KCl=0.565 approx.

The reason of the difference of 0.125 volt between this and the value found by the KCN null solution is suggested by

inspection of the electrocapillary curves.

The maxima for the KCN solutions are lower than those for the KCl solutions of corresponding strength, and the "horizontal distance" between the curves after they become parallel is approximately 0·125 volt greater than the distance between the maxima. Consequently (cf. Phil. Trans. l. c. p. 67) the solution at the maximum surface-tension in KCN is 0·125 volt more positive to the mercury than it is at the maximum in KCl.

§ 11. Every solution for which the maximum of the electrocapillary curve is at the origin is a null solution, but the potential-differences between mercury and different null solutions will be different if the maxima for these solutions are not the same.

If traces of other substances can be added to a n/4 KCl solution in such a way as to move the maximum of the electrocapillary curve to the origin without appreciably raising or depressing it, then such a solution will be about 0.125 volt less positive to mercury than the null solution of n/4 KCN. This null solution when measured against pure n/4 KCl will give an E.M.F. of 0.565 in place of the E.M.F. of 0.69 given by the n/4 KCN null solution. Hence, if Palmaer's solutions were produced from n/10 KCl without appreciable alteration of the maximum, the difference between his results and ours is immediately explained.

§ 12. Effect of Na<sub>2</sub>S on the p.d. between Hg and KCl.— The p.d. between mercury and an electrolyte is controlled, according to the theory of Nernst, by the concentration p of the mercury ions in solution. If  $\pi$  is the potential rise from the solution to the mercury, then

$$\partial \pi/\partial p = kT/p$$
, . . . . (i.)\*

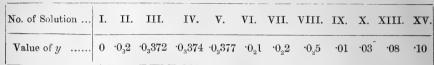
where T is the absolute temperature and k is a constant. The rise can therefore be diminished by decreasing p. From Palmaer's experiments and others (e. g., Behrend, Zeits f. phys. Chem. xi. p. 481, 1893), it can be inferred that a large diminution of p is produced by saturating a KCl solution in contact with mercury with  $H_2S$ . We therefore thought it likely that by addition of  $Na_2S$  to the KCl solution it would be possible to move the electrocapillary curve to the right, i. e. so that the maximum approached the origin. It remained to determine by experiment the relative amount of  $Na_2S$ 

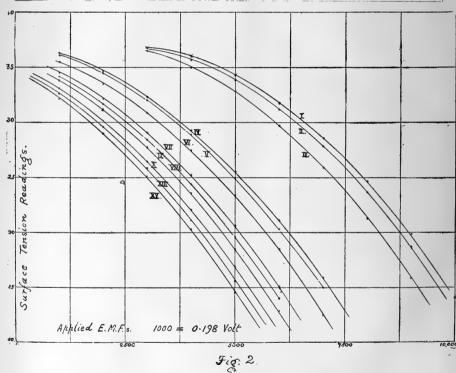
\* An interesting method of deducing a similar equation was given by Professor J. J. Thomson in the Philosophical Magazine for 1895.

necessary for the purpose of reaching the origin. Electrocapillary curves were obtained with solutions containing gradually increasing proportions of Na<sub>2</sub>S. The general composition of the solutions was

$$x(n \text{ KCl}) + y(n \text{ Na}_2\text{S}, 9\Pi_2\text{O}),$$

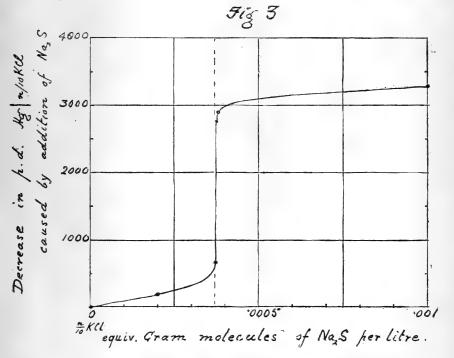
where x+y=0.1; i. e., considering the sum of the contents, the solution was always 1/10th normal, and the content in kations remained approximately constant. Curves were obtained for a number of different values of y. Some of the results are shown in fig. 2, in which the values of y represented are as follows:—





From these results it will be seen that less than  $\cdot 001n \text{ Na}_2\text{S}$  added to  $\cdot 099n \text{ KCl}$  was sufficient to move the maximum of

the electrocapillary curve to the left of the origin. Further, when the value of y was about 00037, an extremely small variation produced a very large change in the position of the maximum. This is represented in fig. 3, which shows how the displacement of the descending branch of the electrocapillary curve depends on the percentage composition of the n/10 solution. Since the concentration in kations was the same for all solutions, this curve represents (Phil. Trans.  $l.\ c.\ p.\ 80$ ) how the potential of the solution with respect to the mercury rises with increase in the amount of the sulphide.



§ 13. The extremely rapid concentration variation of the potential near y=00037 was very inconvenient for our purpose, for it happened that the solution which we sought, i.e. one having its electrocapillary maximum at the origin, would contain an amount of sulphide corresponding approximately to this value of y. The experiments of Behrend (l.c.p.481) suggested that the rapid variation of potential at a critical value of y occurred near the completion of the conversion of feebly soluble chloride of mercury into still

less soluble sulphide. Thus, assuming c to represent the concentration of  $\mathrm{Hg_2Cl_2}$  in solution before addition of  $\mathrm{Na_2S}$ , if the amount of sulphide added were (c-c'), i. e. less than c, we might have (see however § 15):—

$$c Hg_2 Cl_2 + (c - c') Na_2 S = c' Hg_2 Cl_2 + (c - c') Hg_2 S + 2(c - c') NaCl.$$

Assuming  $\alpha$  and  $\beta$  to represent the fractions of the chloride and sulphide respectively, which are electromotively active, the ionic concentration p of the mercury in solution would be

$$p = 2\alpha c' + 2\beta(c - c')$$
, and hence  $\partial p/\partial c' = 2(\alpha - \beta)$ .

Then, from equation (i.) above, we should have

$$\partial \pi / \partial c' = k \mathbf{T}(\alpha - \beta) / (\alpha c' + \beta \overline{c - c'}).$$

From this it is seen that if  $\beta$  is very small compared with  $\alpha$ , the value of  $\partial \pi/\partial c'$  will become very large when c' becomes very small, i.e. when the amount of Na<sub>2</sub>S added is very nearly equivalent to the amount of Hg<sub>2</sub>Cl<sub>2</sub> in solution.

§ 14. When the amount of  $Na_2S$  added is in excess of the

Hg<sub>2</sub>Cl<sub>2</sub> in solution we may have

$$c\mathrm{Hg_2Cl_2} + (c+c')\mathrm{Na_2S} = c\mathrm{Hg_2S} + c'\mathrm{Na_2S} + 2c\mathrm{NaCl}.$$

From this it is seen that the potential of the liquid with respect to the electrode will continue to rise when, after the whole of the chloride is decomposed, more and more Na<sub>2</sub>S is added. For, assuming the law of mass action, the ionic concentration of the Hg obtained from the Hg<sub>2</sub>S will diminish when, by introduction of further quantities of Na<sub>2</sub>S, the concentration of the S ions in solution is raised.

Suppose now that to a solution containing an excess of  $Na_2S$  a small quantity 2c'' of an acid HX is added. Then we shall get

$$\begin{split} c H g_2 C l_2 + (c + c') N a_2 S + 2 c'' H X \\ = c H g_2 S + (c' - c'') N a_2 S + c'' H_2 S + 2 c'' N a X + 2 c N a C l. \end{split}$$

Now if we assume the coefficients of ionization of the Na<sub>2</sub>S and the H<sub>2</sub>S to be  $\gamma$  and  $\delta$  respectively, the concentration of S ions arising from these two substances will be  $\gamma(c'-c'') + \delta c''$ ; while, before the addition of the acid, the concentration of S ions arising from the Na<sub>2</sub>S would exceed  $\gamma c'$ . The value of  $\delta$  will in general be less than that of  $\gamma$ , because, in moderately dilute solution, H<sub>2</sub>S is a very poor conductor compared with Na<sub>2</sub>S. Therefore addition of the

acid HX will reduce the concentration of the S ions in the solution containing  $c\mathrm{Hg}_2\mathrm{S}$ , and will in consequence cause the concentration of the Hg ions to rise. Thus addition of the acid will tend to reduce the effect of the Na<sub>2</sub>S and will cause the electrocapillary curve to move towards the right.

Hence, if too much  $Na_2S$  has been added, so that the maximum is to the left of the origin, it may be possible to obtain a null solution by the addition of a small quantity of an acid. Moreover, it may be of advantage experimentally to proceed in this way by overshooting the mark and then adding acid, rather than by attempting to hit it by reducing the amount of  $Na_2S$ . For, as can be seen, the rate at which the curve will move towards the right will be less when a small quantity of acid is added than when an equivalent quantity of sulphide is taken away. Thus, when the acid is absent, the concentration  $p_s$  of S ions, outside the  $Hg_2S$ , is such that  $\partial p_s/\partial c'$  exceeds  $\gamma$ ; but when the acid is added

$$\partial p_s/\partial c^{\prime\prime} = -(\gamma - \delta).$$

§ 15. It is not contended for the above equations that they necessarily do more than indicate the course of events. The Na<sub>2</sub>S used probably contained traces of higher sulphides, and the chemical relations between the substances concerned are complicated. The final product of the action of Na<sub>2</sub>S on the mercury in solution would no doubt be a double sulphide of HgS and Na<sub>2</sub>S, and it is worth notice with regard to this that, after the very rapid change at '00037n Na<sub>2</sub>S, the potential of the electrode continued to decrease fairly rapidly until about '002n Na<sub>2</sub>S had been added. The rate of decrease fell comparatively suddenly at this point, and for subsequent additions of Na<sub>2</sub>S (until the whole of the KCl was replaced) remained very small.

The concentration of mercurous ions in a solution of KCl standing over mercury and calomel has been estimated indirectly by Behrend and others, and from the values obtained it would appear that, if the above interpretation of our observations is correct, only a small fraction of the mercury in solution can be in the ionized condition. It is important to note, however, that the comparatively large value of the solubility of Hg<sub>2</sub>Cl<sub>2</sub>, to which the results of § 12 seem to lead, may on account of the influence of dissolved atmospheric oxygen be more apparent than real. It is commonly agreed that the interaction between Hg and a solution of a chloride, from which the existence of Hg<sub>2</sub>Cl<sub>2</sub> in the solution results, occurs through the intervention of the oxygen dissolved in the latter. This interaction will

continue (1) until the solution becomes saturated with Hg<sub>2</sub> Cl<sub>2</sub>, or (2) until the supply of oxygen near the electrode is used up. In the latter event, further formation of Hg, Cl. would cease until, by diffusion, a fresh supply of oxygen approached the electrode. Since, however, the solubility of oxygen in n/10 KCl is probably much greater than that of Hg<sub>2</sub>Cl<sub>2</sub>, it is probable that the interaction terminates in accordance with the first of the alternatives and before the whole of the oxygen per c.cm. near the electrode is removed. If now a small quantity of Na<sub>o</sub>S is added to the solution it will precipitate the whole or a part of the Hg2 Cl2 with which the solution is saturated. But the further solution of Hg, Cl, will be possible by interaction between the mercury, the KCl in the solution and the excess of dissolved oxygen. In fact the complete removal of Hg<sub>2</sub> Cl<sub>2</sub> from solution by means of Na, S, as represented in the equations given in §§ 13, 14, will not be possible until the whole of the dissolved oxygen is used up.

From this point of view, what happens when an aerated solution of KCl containing Na<sub>2</sub>S is poured upon mercury may be described, figuratively, as a competition between the salts for the oxygen and mercury in the surface layer. Since any Hg<sub>2</sub>Cl<sub>2</sub> formed before the removal of the Na<sub>2</sub>S is complete will be at once decomposed by the latter and precipitated as sulphide, the net result of this competition is that the KCl can only interact permanently with such oxygen as the Na<sub>2</sub>S leaves uncombined. The critical amount of the

latter is reached when it leaves none \*.

In any attempt to form a complete picture of the process, however, it would be necessary to take account of possible difference in the subsequent rates of approach of Na<sub>2</sub>S and O to the surface layer, from above, by diffusion and convection. This would lead us too far from our present aim.

The exact composition of our critical Na<sub>2</sub>S solution was uncertain, and the further study of the question presented chemical difficulties which it did not seem profitable to inves-

tigate with the materials at our disposal.

§ 16. Null Solution of KCl.—The argument developed above proved successful as a working hypothesis. An n/10 KCl solution containing 001n Na<sub>2</sub>S was first made up, and others containing different amounts of acetic acid (suggested by Palmaer's experiments) were then obtained

<sup>\*</sup> Some results of experiments still in progress in connexion with this view were indicated when the paper was read.

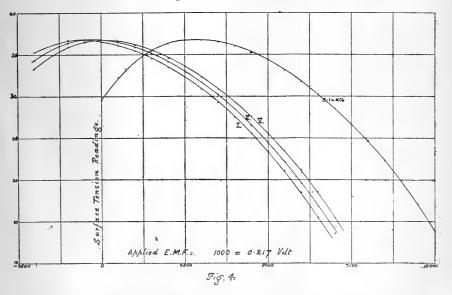
# Potential Differences determined by Null Solutions. 491

from it. The results of the experiments with these solutions are summarized below:—

	1.	2.	3.	4.	5.	6.	7.
,	Strength of acetic acid.		E.M.F. for Max. S.T. (volt.)	Horizontal distance to $\frac{n}{10}$ KCl curve.	$\left  \text{ sol. } \right  \frac{n}{10} \text{ KCl } \left  + \right $	sol.   + (volt.)	$\downarrow$ sol. $\left[\frac{n}{10} \text{ KCl}\right] + \left(\text{volt.}\right)$
I	0	36.82	- 123	.661	·660 `	129	.564
ιι	$\cdot 0011 \; n$	36.81	051	622	618	049	•560
п	·0017 n	36.84?	020	.588	•582	018	·56 <b>4</b>
V	0023 n	36.80	005	.578	·571	009	.564
v	0028 n	36.80	·010	•568	•562	.005	•562
7 <b>I</b>	·0040 n	36.80	·020	.556	•549	·016	•564

36.80 = Maximum S.T. for n/10 KCl.

The numbers representing the normality in acetic acid are only approximate. Nothing turns upon the accuracy of their determination. Some of the corresponding electrocapillary curves are shown in fig. 4.



The measurements are less exact than in the case of the KCN curves. Owing no doubt to the presence of small

quantities of dissolved oxygen, the p.d. between the large Hg electrode and the solution sometimes changed perceptibly during the short time required to determine the electrocapillary curve. It will be seen, however, that a series of curves with practically equal maxima of surface-tension was now obtained. The null solution lies between IV. and V., and corresponds within the limits of experimental error with a solution of which the maximum of the electrocapillary curve is at the origin. Part of the difference between the numbers in columns 4 and 5 was certainly due to increase with time of the p.d. Hg | solution. The capillary curves were taken first and are not exactly parallel to the decinormal KCl curve. The distance decreases slightly towards the lower ends of the curves. The p.d. between the strongest of the solutions and the n/10 RCl solution was probably less than a millivolt (cf. Palmaer, Zeit. p. Chem. I. c. 1907, p. 155).

By examination of the data for solutions IV. and V. it is seen that a null solution of the present kind, interpreted according to the assumptions of Palmaer, would give, for the p.d. Hg | n/10 KCl, a value agreeing with his result. But, as will be seen, his assumption of zero p.d. between Hg and the null solution is not at all necessary. The only necessary conclusion is that the p.d. between the still Hg and the solution is the same as that between the dropping

Hg and the solution.

From the data in the Table it is seen that, for reasons already given, the maxima being practically equal in all the solutions, the p.d. between the dropping electrode and the solution should be in every case the same. This result is probably of significance in the theory of electrocapillarity. Its truth is shown by the practical equality of all the numbers in Column 7.

§ 17. Effect of Oxygen upon Paschen's relation.—With respect to the data in columns 3 and 6, § 16, showing the fulfilment of the Paschen relation for the present series of electrolytes, it is important to state that the dropping-electrode experiments were performed in an atmosphere of hydrogen (cf. § 7, above). A piece of wide glass tubing open at both ends encircled the dropping electrode. The lower end of this tube was immersed in the electrolyte, and the upper was closed by a rubber cork in which were three holes. The drop electrode passed through the central hole: the others served for the inlet and outlet of the hydrogen respectively.

The following data are given as examples of the necessity for the exclusion of air. In one case, the maximum of the capillary curve being  $+\cdot01$  volt, a Paschen electrode against still mercury in the same solution showed  $-\cdot05$  volt, increasing to  $-\cdot07$  when the mercury jet was partially immersed. The solution quickly became cloudy and the mercury tarnished so rapidly that it fell as a dirty powder.

In another experiment the jet was surrounded by hydrogen, the water used in preparing the solution having been recently boiled to decrease the amount of dissolved air. Before complete displacement of the air by hydrogen, the Paschen electrode E.M.F. was  $-\cdot024$  volt. It fell gradually to  $-\cdot014$  volt and then remained constant. The mercury fell quite clean. Some of the solution was now withdrawn, and its electrocapillary curve was determined. The maximum lay at  $-\cdot015$  volt.

In a third experiment, the jet being surrounded by hydrogn, the electrode E.M.F. was -024, agreeing with the electrocapillary maximum. Oxygen was now admitted and displaced the hydrogen. The Paschen electrode E.M.F. became -140. With the jet partially immersed the E.M.F.

increased to -.240.

Various experiments with other gases and with insulating liquids were tried, e. g., it was found that the Paschen relation was, under certain conditions, fulfilled when air was replaced by benzene; but further description of these experiments is omitted from consideration of space.

§ 18. Inferences from results obtained with Null Solutions of KCN and of KCl.—Summarizing the results of the two series of experiments described, it is seen that, with respect to the p.d. Hg | electrolyte as considered by Palmaer, there are two kinds of null solution. One is formed by the addition to the electrolyte of very small quantities of certain substances which leave the shape of the electrocapillary curve unaltered, with the maximum undepressed, but move it parallel to itself towards the left. This kind of null solution, interpreted in the way described by Palmaer, will give the result that the p.d. is zero at the maximum of the electrocapillary curve.

A second kind of null solution is obtained by using a different electrolyte and altering its concentration until the maximum of the capillary curve is at the origin. This kind may have a depressed maximum compared with the original electrolyte, KCl for example, and will in that case give a value, for the p.d. Hg | KCl, greater than that obtained by

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Palmaer if the measurements are interpreted in the way he describes. If, on the other hand, the curve for the null-solution electrolyte has a higher maximum than the corresponding curve for KCl, then the p.d. Hg | KCl found by Palmaer's method will be less than that which he gives. We have not attempted to find a null solution exactly of this last kind, although it is known that the electrocapillary maximum of a saturated KOH solution is near the origin and is considerably higher (Phil. Trans. l. c. p. 68) than that of concentrated KCl.

We have, however, obtained null solutions by the addition of small quantities of  $\rm Na_2S$  (and acetic acid) to  $n/10~\rm KI$  solution, which has a very depressed maximum, and to  $n/10~\rm KOH$  solution, which has a higher maximum than  $n/10~\rm KCl$ . The results of these experiments exhibit the

truth of the conclusions we have drawn.

§ 19. Null Solution of KI.—The attempt to obtain a null solution from n/10 KI succeeded approximately when the composition of the solution was about 001n Na<sub>2</sub>S + 099nKI. The maximum surface-tension occurred when the applied E.M.F. was -01 volt. It was unnecessary for our purpose to obtain a nearer approximation to a null solution. The E.M.F. between a dropping electrode falling through hydrogen into this solution and a still electrode was at first imperceptible. After some time it was 006 volt. Mercury in this solution measured against mercury in n/10 KCl gave an E.M.F. of 793 volt. A fresh null solution of KCl, made up by trial for comparison, measured against n/10 KCl in the same way gave 565 volt. The two solutions measured against each other gave 228 volt. The results of the measurements are tabulated below:—

,						
1.	2.	3.	4.	5,	6.	7.
Null Solution.	Max. S.T. (scale-	E.M.F. for max. S.T.	Horizontal distance to $\frac{n}{10}$ KCl curve.	$\int \operatorname{sol.} \left[ \frac{n}{10} \operatorname{KCl} \right] +$	sol. +	null   null   +
	reading).	volt.	volt.	volt.	volt.	<b>v</b> olt.
$\frac{n}{10} \text{ KI} + \frac{n}{1000} \text{Na}_2 \text{S}$	28.85	01	· <b>7</b> 89	793	0	
$ \frac{n}{10} \text{ KCl} + x \text{Na}_2 \text{S} \dots $	30.5	- 01	•569	•565	- 01	·228

These experiments show that the p.d. Hg | n/10 KCl cannot be 0.57 unless, interpreting them according to Palmaer's method, the p.d. between n/10 KCl and n/10 KI is nearly a quarter of a volt. Such a potential-difference is impossible according to the theories at present in vogue (cf. Phil. Trans.  $l.\ c.\ p.\ 62$ ).

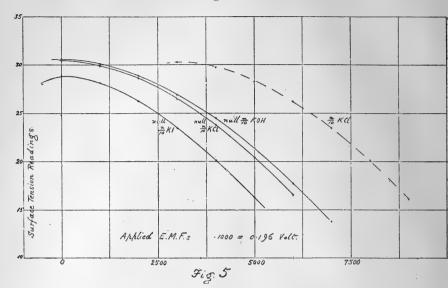
§ 20. Null Solution of KOH.—In attempting to obtain a null solution from n/10 KOH it was found that the addition of Na<sub>2</sub>S ( $\cdot 001n$  to  $\cdot 002n$ ) produced a gradual shift of the maximum to the left which continued over a long time. A solution with the maximum at the origin could not be obtained conveniently with Na<sub>2</sub>S alone on account of this time effect It was found however that if, after the solution had stood for some time over the mercury, dilute acetic acid was added drop by drop and the solution stirred, the maximum could be brought from the left to zero and the time effect was now negligible. The results of the experiments with this null solution are given below:—

1.	2.	3.	4.	5.	6.
Null Solution.	Max. S.T. (scale- reading).	E.M.F. for max. S.T.		$\begin{bmatrix} \text{null.} \\ \text{sol.} \end{bmatrix} \frac{n}{10} \text{ KOl } \end{bmatrix} +$	null   +
	rouding).	volt.	volt.	volt.	volt.
$\frac{n}{10}$ KOH					
+Na <sub>2</sub> S	30.61	+.01	·515	•509	.008
+HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>				•	

In considering the value 0.509 volt in column 5 it has to be remembered that there is now an appreciable p.d. between the solutions. Its value calculated in the usual way is  $n/10 \text{ KOH} \mid n/10 \text{ KCl} = 0.016$  volt at 20° C.; and consequently we now obtain, according to Palmaer's method, Hg  $\mid n/10 \text{ KCl} = 525$  volt. But, according to the interpretation we have offered, this result signifies only that the potential reckoned from the solution to mercury at the maximum is about 04 volt less in the case of n/10 KOH than in that of n/10 KCl. A result which, as before, is in agreement with the forms and relative positions of the electrocapillary curves.

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The electrocapillary curves for the null solutions of KI and of KOH are shown in fig. 5.



The results of our experiments may be summarized as follows:—

# § 21. Summary of Conclusions.

1. The potential-differences between different null solutions and mercury are not the same. This is proved, allowing for the contact p.d. between electrolytes, by measuring each p.d. against the p.d. Hg | KCl, and also by measuring one null solution against another. The result is also deducible from the electrocapillary curves alone, without introduction of the question of the p.d. between electrolytes.

2. If the null-solution potential-differences are assumed to be zero, the values obtained for the p.d. Hg | n/10 KCl vary from about 0.53 volt to 0.79 volt. Assuming that the p.d. at the electrocapillary maximum is most likely to be zero when the maximum is undepressed, it is probable that the

p.d. Hg | n/10 KCl does not exceed 0.53 volt.

3. The polarizing E.M.F. required to produce the maximum surface-tension between mercury and a given electrolyte has been proved by Paschen to be equal, in many cases, to the E.M.F. of the corresponding dropping-electrode circuit. This relation is shown to be true in four particular cases in which each E.M.F. is equal to zero. It is also shown that

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in none of these cases is the p.d. Hg | electrolyte necessarily zero.

4. It is shown that the Paschen relation immediately fails when the chemical action at the drop-electrode due to

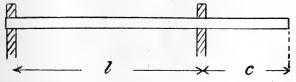
atmospheric oxygen becomes appreciable.

5. The Paschen E.M.F. between mercury and a solution of KCl remains unchanged on the addition to the solution of small quantities of Na<sub>2</sub>S, although the natural p.d. between mercury and the KCl solution is thereby altered by more than half a volt.

6. A critical percentage of  $Na_2S$  was found for which the natural p.d. just mentioned altered with extreme rapidity as in the cases studied by Behrend, in which he observed the variation of the E.M.F.,  $Hg \mid Hg_2(NO_3)_2 \mid Hg$ , produced by the gradual addition of KCl or KBr at one electrode. In the present case the change in the p.d.  $Hg \mid$  electrolyte was deduced directly from the electrocapillary curves.

XLVI. On the Lateral Vibration of Bars supported at Two Points with One End overhanging. By John Morrow, M.Sc., D.Eng.; Lecturer in Engineering, Armstrong College (University of Durham)\*.

WHEN a bar is carried on two supports and has one end overhanging by an amount c, as shown in the figure,



its natural period of vibration is to be determined from the equation

 $(\cosh ml \sin ml - \sinh ml \cos ml) (\cosh mc \sin mc - \sinh mc \cos mc) - 2 \sinh ml \sin ml (1 + \cosh mc \cos mc) = 0,$ 

in which

 $m = (2\pi N)^{\frac{1}{2}} (\rho \omega / EI)^{\frac{1}{4}};$ 

E = Young's Modulus for the material;

I = the moment of inertia of the section about an axis perpendicular to the plane of bending;

 $\omega$  = sectional area of bar (assumed uniform);

 $\rho = \text{density of material};$ 

N = frequency of natural vibrations.

\* Communicated by the Physical Society: read November 8, 1907.

For given ratios c/l we can obtain values of ml from the above equation. This has been done incidentally by Professor Dunkerley in connexion with his work on the whirling of shafts \*, but the calculations were not sufficiently extended to give very accurate results. By comparison with the table given below, it will be seen that the approximate formula used by Dunkerley cannot be relied on to give more than the first two significant figures.

Having recently required more accurate solutions, I have found it necessary to make a more elaborate calculation, and as the results have been obtained to six figures it appears

desirable to place them on record.

If we write a for c/l and  $\theta$  for ml, and expand each term of the equation in ascending powers of  $\theta$  and  $a\theta$ , we get, as far as the twenty-first powers,

$$4\theta^{2} - (\cdot 0\dot{4} + \cdot \dot{4} \, a^{3} + \cdot \dot{3} \, a^{4})\theta^{6} + (\cdot 000035273369 + \cdot 0\dot{0}2116\dot{4} \, a^{3} + \cdot 0\dot{0}3\dot{7} \, a^{4} + \cdot 0\dot{0}2116\dot{4} \, a^{7} + \cdot 00\dot{0}7936\dot{5} \, a^{8})\theta^{10} - (\cdot 58730 + 106\cdot 8890 \, a^{3} + 293\cdot 945 \, a^{4} + 1007\cdot 811 \, a^{7} + 881\cdot 834 \, a^{8} + 106\cdot 889 \, a^{11} + 26\cdot 722 \, a^{12})10^{-8}\theta^{14} + (\cdot 033 + 13\cdot 2 \, a^{3} + 49 \, a^{4} + 508\cdot 8 \, a^{7} + 700 \, a^{8} + 509 \, a^{11} + 297 \, a^{12} + 13\cdot 2 \, a^{15} + 2\cdot 4 \, a^{16})10^{-11}\theta^{18} = 0.$$

Assuming values of a and calculating  $\theta$  we obtain the numbers tabulated below:—

Ratio $c/l$ .	Value of $\theta$ .	
Unity	1.50592	
Three-quarters	1.90170	
One-half	2.51895	
One-third	2.94042	
One-quarter	3.05881	
One-fifth	3.09975	
One-sixth	3.11752	
One-seventh	3.12647	
One-eighth	3.13148	
One-ninth	3.13449	
One-tenth	3.13641	
Zero	3.14159	

<sup>\*</sup> Phil. Trans. A, 1894, p. 279.

Dr. Chree has given the following approximate formula for use when c/l is small \*:—

$$ml = \pi (1 - \frac{1}{6}\pi^2 c^3/l^3)$$
.

It is stated to be satisfactory so long as  $(c/l)^3\pi^3/6 \coth \pi$ is small compared with unity. As a matter of fact we find that, when c/l is one-sixth, Chree's formula is correct to within 0.005 per cent., and the error is less than one per cent. even when c/l is one-half.

The number of vibrations per second is given by the

formula

$$N = \frac{\theta^2}{2\pi} \sqrt{\frac{EI}{\rho \omega l^4}}.$$

September 1907.

XLVII. An Experimental Examination of Gibbs's Theory of Surface-Concentration, regarded as the basis of Adsorption, with an Application to the Theory of Dyeing. (From the Muspratt Laboratory of Physical and Electrochemistry, University of Liverpool.) By W. C. M. Lewis, M.A.+

#### CONTENTS.

I. Object of the investigation; the characteristics of Adsorption Phenomena.

II. Theoretical Discussion; Gibbs's Theory of Surface Concentration; Milner's Calculations.

III. Experimental Methods and Apparatus; Results.

IV. Application to the Theory of Dyeing.
V. Summary.

# I. Object of the Investigation.

NDER the term "Adsorption" are grouped phenomena which may be regarded as forming an intermediate stage between chemical combination on the one hand, and true absorption or solution on the other. Different types of Adsorption have been studied, but in general a solid substance (e.g. charcoal) has been utilized as the adsorbent body.

The present paper is an account of an experimental attempt at measuring adsorption effects quantitatively and interpreting the values obtained in the light of Gibbs's theory of surfaceconcentration. The treatment is novel in that the adsorption has been measured at a liquid-liquid interface; for it is only when dealing with liquid interfaces (or surfaces) that it is

<sup>\*</sup> Phil. Mag. [6] vol. vii. p. 517, May 1904.

<sup>†</sup> Communicated by the Physical Society; read February 28, 1908.

possible to measure interfacial- or surface-tension—a fundamental factor in the thermodynamic consideration of the question.

# The Characteristics of Adsorption Phenomena.

The earlier investigations on adsorption dealt in general with the adsorption of gases on the surfaces of various solid materials. The case of vapours is of much more recent date. the most important instances being those of Travers\* and Trouton †. Modern investigators have, however, dealt chiefly with the question of the adsorption of dissolved substances at the surface of some solid body in contact with the solution. Among the numerous recent memoirs on the subject may be mentioned those of Küster !, Schmidt &. Walker & Appleyard ||, Biltz ¶, Lagergren \*\*, and in particular Freundlich ††. Freundlich's investigations contain the most systematic and accurate determinations yet recorded of the adsorption at a charcoal surface of a series of organic substances in aqueous solution. The general method was to prepare a solution of a certain substance (say a dye-stuff), and to a known volume of this solution to add a certain quantity of very finely powdered pure blood-charcoal. A certain amount of the dye is removed by the charcoal, the change in concentration being determined colorimetrically.

Among Freundlich's most important results may be mentioned that the equilibrium state is reached exceedingly rapidly—in about five seconds; that, using the same solid body the quantity adsorbed varies with the chemical constitution of the solute, e.g. aromatic acids are adsorbed in greater quantity than aliphatic; and finally, that the effects

differed with the solvent used.

We may sum up the characteristics of adsorption which differentiate it from chemical combination thus:—

- (1) The order in which a series of dissolved substances are adsorbed does not differ even when one substitutes as the adsorbing material, bodies as unlike as charcoal, silk, clay, and cotton. This is unlikely on the assumption of chemical combination.
- \* Travers, Proc. Roy. Soc. series A, vol. lxxviii. p. 9 (1907). † Trouton, Proc. Roy Soc. series A, vol. lxxvii. p. 292 (1906). ‡ Küster, Zeitschrift Phys. Chemie, vol. xiii. p. 445 (1894).

§ Schmidt, Zeit. Phys. Chem. vol. xv. p. 60 (1894).

| Walker & Appleyard, Journ. Chem. Soc. vol. lxix. p. 1334 (1896).
| Biltz, Ber. d. deut. chem. Gesell. vol. xxxvii. p. 1706 (1904);
vol. xxxviii. p. 2963 (1905).

\*\* Lagergren, Zeit. Phys. Chem. vol. xxxii. p. 174 (1900).

†† Freundlich, Zeit. Phys. Chem. vol. lvii. p. 385 (1906); vol. lix. p. 284 (1907).

(2) The reaction goes to an end almost instantaneously.

(3) Heat effects, even in concentrated solutions, are undetectable. Chemical action, on the other hand at relatively low temperatures is usually accompanied by evolution of heat.

# Characteristics which distinguish Adsorption from Absorption.

The difference existing here (which has been attested by numerous determinations) may be stated thus: There is not a direct proportionality between the concentration of the solution or partial pressure of the solute and the amount adsorbed. To take an example from Walker and Appleyard's \* paper on the adsorption of picric acid at the surface of silk.

The quantities of picric acid (remaining after the reaction) in the aqueous solution and in the silk itself are estimated,

the following being the results obtained :-

TABLE I.

rams Picric Ac 1 c.c. solution.	i	n 1 gram s	silk.		Ratio $\frac{a}{b}$
(a)		(b)	¢		
0.064	į	. 13		E h	0.002
1.98	{	37			0.023
7.0		75			0.094

Assuming the molecular weight of the picric acid to be the same in water and silk, the ratio  $\frac{a}{b}$  should have been constant had true absorption taken place.

## II. THEORETICAL DISCUSSION.

# Gibbs's Theory of Surface Concentration.

A theoretical investigation of this subject from the standpoint of thermodynamics forms one of the chapters in Gibbs's † memoir on "Equilibrium in Heterogeneous Systems." He

<sup>\*</sup> Walker & Applevard, loc. cit.

<sup>† &#</sup>x27;Scientific Papers of J. Willard Gibbs.' English edition, vol. i. p. 219.

first takes up the consideration of the mass or bulk equilibrium of a heterogeneous system, i.e. equilibrium in which any surface phenomenon is of insensible magnitude, and then proceeds to examine the case in which the surface area is relatively large and the influence of surfaces of discontinuity upon the equilibrium of heterogeneous masses becomes of importance. To use his own words:—

\*"The solution of the problems which precede may be regarded as a first approximation in which the peculiar state of thermodynamic equilibrium about surfaces of discontinuity is neglected. To take account of the condition of things at

these surfaces, the following method is employed:—

"Let us suppose that two homogeneous fluid masses are separated by a surface of discontinuity, i.e. by a very thin non-homogeneous film. Now we may imagine a state of things in which each of the homogeneous masses extends without variation of the densities of its several components, or of the densities of energy and entropy, quite up to a geometrical surface (to be called the dividing surface) at which the masses meet. We may suppose this surface to be sensibly coincident with the physical surface of discontinuity.

"Now if we compare the actual state of things with the supposed state, there will be in the former in the vicinity of the surface a certain (positive or negative) excess of energy, of entropy, and of each of the component substances. These quantities are denoted by  $\epsilon^s$ ,  $\eta^s$ ,  $m_1^s$ ,  $m_2^s$ , etc., and are treated as belonging to the surface. The s is simply used as a distinguishing mark, and must not be taken for an algebraic

exponent.

"It is shown that the conditions of equilibrium already obtained relating to the temperature and the potentials of the homogeneous masses are not affected by the surfaces of discontinuity, and that the complete value of  $\delta e^s$  is given by the equation

$$\delta \epsilon^s = t \delta \eta^s + \sigma ds + \mu_1 \delta m_1^s + \mu_2 \delta m_2^s + \text{etc.}$$

in which s denotes the area of the surface considered, t the temperature,  $\mu_1$   $\mu_2$  etc. the potentials for the various components in the adjacent masses...."

"The quantity  $\sigma$  we may regard as defined by the [above] equation itself or by the following:

$$\epsilon^s = t\eta^s + \sigma s + \mu_1 m_1^s + \mu_2 m_2^s + \text{ etc.}$$

<sup>\*</sup> Gibbs, 'Scientific Papers,' vol. i. p. 365.

from which by differentiation and comparison with the former we obtain

$$d\sigma = -\eta_s dt - \Gamma_1 d\mu_1 - \Gamma_2 d\mu_1 - \text{ etc.},$$

where  $\eta_s$ ,  $\Gamma_1$ ,  $\Gamma_2$ , etc. are written for

$$\frac{\boldsymbol{\eta}^s}{s}$$
,  $\frac{m_1^s}{s}$ ,  $\frac{m_2^s}{s}$ , etc.,

and denote the superficial densities of entropy and of the various substances. We may regard  $\sigma$  as a function of t,  $\mu_1$ ,  $\mu_2$ , etc., from which, if known,  $\eta_s$ ,  $\Gamma_1$ ,  $\Gamma_2$ , may be determined in terms of the same variables. An equation between  $\sigma$ , t,  $\mu_1$ ,  $\mu_2$ , etc. may therefore be called a fundamental equation for the surface of discontinuity."

The final equation obtained above has been simplified and

applied by Gibbs \* to an actual case, viz.:-

"If liquid mercury meet the mixed vapors of water and mercury in a plane surface, and we use  $\mu_1$  and  $\mu_2$  to denote the [chemical] potentials of mercury and water respectively and place the dividing surface so that  $\Gamma_1 = 0$ , i. e., so that the total quantity of mercury is the same as if the liquid mercury reached this surface on one side and the mercury vapor on the other, without change of density on either side, then  $\Gamma_{2,1}$  will represent the amount of water in the vicinity of the surface above that which there would be if the water-vapor just reached the surface without change of density, and this quantity (which we may call the quantity condensed [i. e., adsorbed] upon the mercury) will be determined by the equation

$$\Gamma_{\scriptscriptstyle 2,1} = -\frac{d\sigma}{d\mu_{\scriptscriptstyle 2}}.$$

In this equation and the following, the temperature is constant and the surface of discontinuity plane.

"If the pressures in the mixed vapors conform to the law of Dalton, we shall have for constant temperature

$$dp_2 = cd\mu_2$$
;

 $p_2$  denotes the part of the pressure in the vapor due to the water-vapor, and c the density of the water-vapor. Hence

$$\Gamma_{2,1} = -c \frac{d\sigma}{dp_2} \quad \bullet \quad \cdots \quad \bullet \quad "$$

<sup>\*</sup> Gibbs, 'Scientific Papers;' vol. i. p. 235.

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Now applying the gas law P = RTc, finally we obtain

$$\Gamma_{2,1} = -\frac{c}{RT} \frac{d\sigma}{dc}$$
.

This equation is of fundamental importance in that, if we assume its applicability to adsorption measurements, it contains the relationships between bulk-concentration, surface-tension, and quantity adsorbed in an experimentally determinable form.

The same expression may be obtained more simply as follows:—\*

Consider the equilibrium at a surface (say of solid or liquid) in contact with a solution.

Let  $\sigma = \text{surface-energy per unit of surface.}$ 

s =area of surface exposed to the solution.

m<sup>s</sup> = the mass of solute adsorbed at the surface of the solid *in excess* of that normally present.

The temperature is supposed to be constant.

U = total energy of the heterogeneous film per unit of surface.

U can be increased:-

(1) by increasing the surface area, in which case the work required =  $\sigma ds$ ;

(2) by increasing the concentration of the solute in the interfacial layer. This is proportional to  $dm^s$  namely  $\mu dm^s$ , where  $\mu$  is the chemical potential of the solute.

Then  $dU = \sigma ds + \mu dm^s$ ,

$$\therefore d(\mathbf{U} - \boldsymbol{\mu} m^s) = \boldsymbol{\sigma} ds - m^s d\boldsymbol{\mu}.$$

And since  $d(U - \mu m^s)$  is a complete differential, we have

$$-\left(\frac{d\sigma}{d\mu}\right)_{s} = \left(\frac{dm^{s}}{ds}\right)_{\mu},$$

but  $\frac{dm^s}{ds}$  = mass adsorbed per unit area of surface, i. e. = I';

$$\therefore \quad \Gamma = -\frac{d\sigma}{d\mu}.$$

Now since

$$d\mu = RT \frac{dc}{c},$$

where  $c \Rightarrow$  the concentration of the solute in the bulk of the solution,

<sup>\*</sup>I am indebted to Prof. W. B. Morton for this deduction.

it follows that

$$\Gamma = -\frac{c}{RT} \frac{d\sigma}{dc}.$$

Note.—It should be noted that the expression obtained above occurs in Freundlich's paper already referred to. From the nature of his experiments it has been quite impossible to attempt a verification experimentally.

We have now to prepare a solution of certain strength c and measure the quantity adsorbed  $\Gamma$  as well as the value of  $\frac{d\sigma}{dc}$ . On substitution of the values in the equation we may obtain a verification or otherwise of the expression \*. It may be stated at once that the results of experiments to be detailed do not show equality on the two sides of the equation—the discrepancy being always in the direction of  $\Gamma$  being many times greater than  $\frac{c}{RT}\frac{d\sigma}{dc}$ .

#### III. EXPERIMENTAL METHODS.

Use of a Liquid-liquid Interface.

As already stated, previous investigations with the exception of Milner's have dealt solely with adsorption at a solid surface—which does not allow of its surface-extent or surface-tension being determined. As it is necessary to evaluate these quantities, the possibility presented itself of measuring the adsorption of a solute at the interface between its solution and another liquid. This latter liquid must of course be absolutely chemically inert towards the solute itself and its solution. Choice fell on a hydrocarbon oil, since a body such as this is characterized by its chemical inertness. The next object was to obtain a substance, preferably soluble in water, which would possess the property of lowering the interfacial tension between water and oil. From their behaviour at the air-liquid interface it seemed likely that the soaps, saponine, and bile-salts would act in

\* While this work was in progress, the results of somewhat similar-determinations were published by Milner (Phil. Mag. Jan. 1907 [6] vol. xiii. p. 96). These referred to equilibrium at the air-liquid surface. He has deduced an identical expression to that already given in this paper, and has applied it to acetic acid in aqueous solution and aqueous sodium oleate. He has found that the actual quantity removed from solution

(r) is nearly ten times the calculated effect  $\left(\frac{c}{RT}\frac{d\sigma}{dc}\right)$ .

Reference might also be made to experiments by Zawidski (Zeit. Phys. Chem. xxxv. p. 77 (1900)) on the formation of the foam produced by the addition of saponine to aqueous solutions of hydrochloric and acetic acids. No measurements applicable to the present case were recorded.

this way at the oil interface. The first experiments to be described were carried out with aqueous solutions of bile-salts.

In order to make certain that no chemical or solubility effects existed between the oil and the solutions, the following tests were carried out:-

(1) A portion of the oil was shaken up with water which was tested with phenolphthalein-neutral reaction, and therefore absence of free fatty acid as impurity.

(2) A portion of the oil was boiled for three hours with reflux condenser with  $\frac{N}{10}$  methyl alcoholic potash—excess potash being titrated with standard acid. It was found that the acid required for neutralization was the same in amount as that for a blank experiment in which no oil was present.

This proves the absence of fatty esters in the oil.

(3) Some of the bile-salt powder was shaken up with the oil, the latter allowed to stand, filtered, and a "drop-number" taken with the pipette (see later) against distilled water. The same drop-number was obtained as with the untreated oil fresh from the stock. Since the tension is a very delicate test for the presence of the salt, the above shows fairly conclusively that there was no salt present in the oil after filtration, i. e., the salt is insoluble in the oil.

(4) The oil was shaken up with a solution of the salt, the oil filtered off and a drop-number taken against water. The same result exactly was obtained as with the oil which had been simply shaken up with distilled water filtered off and a

similar drop number taken against water.

The above tests point conclusively to the fact that no effects of the nature of chemical combination or solubility take place between the oil and the bile-salt.

# Examination of the Bile-salt.

A quantity of "sodium glycocholate" was obtained from Merck. On close examination, however, it appeared that this was far from pure. Besides sodium glycocholate there is also sodium taurocholate and other fatty acid alkali-salts. There were no inorganic substances such as sodium chloride or carbonate. Several determinations of the molecular weight (which is required, as will be seen later) by means of the lowering of freezing-point and rise of boiling-point of water gave as a result 140. Assuming complete dissociation in water, this would give the undissociated molecular weight 280. This latter was confirmed by a determination by the rise of boiling-point of alcohol, the result being 283. The osmotic molecular weight in water (viz. 140) is, however, the quantity required in the subsequent calculations.

Method of measuring the Interfacial Tension.

The Drop-Pipette method was employed, the apparatus

Fig. 1.

B

C

D

E

1

being of the form shown in fig. 1. was first filled with oil (by suction at C) up to the mark E. The tap B was then closed during a determination. The aperture F is carefully wiped before using, and the pipette placed in a fixed position relatively to the solution in all determinations. The bulb D is of about 45 c.c. capacity between E and E<sub>1</sub>. The distance E F is about 8 cms. As soon as the tall jar containing the solution is placed in position, tap A is turned full on, the constriction above only allowing very slow entrance of air; and hence the drops of oil rising through the denser solution are formed with exceeding slowness —at 12 to 15 secs. interval. This, as Lord Rayleigh \* has pointed out, is of great importance in order to obtain fairly accurate determinations; the approximateness of the method being due to the application of a statical theory to what is really a dynamic phenomenon.

The method consisted simply in counting the number of drops formed while the

oil fell from E to  $E_1$ .

Theory of the Drop-Pipette Method.

It may be used in the first instance simply to determine the *relative* tensions of solutions of different concentrations, thus:—

Let V = total volume of oil used,n = total number of drops formed,

then the volume of each drop =  $\frac{V}{n}$ ;

and if  $\rho$  = the density,

the weight of a drop =  $\frac{\nabla \rho}{n}$ .

The tension  $\sigma$  is taken to be proportional to the weight of a drop,

 $\therefore \quad \sigma = K \frac{\nabla \rho}{n}.$ 

<sup>\*</sup> Lord Rayleigh, Phil. Mag. [5] vol. xlviii. p. 321 (1899).

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Similarly for another liquid

$$\sigma_1 = \mathrm{K} \frac{\mathrm{V} \rho_1}{n_1}.$$

Hence

$$\frac{\sigma}{\sigma_1} = \frac{n_1 \rho}{n \rho_1}.$$

As a result of the exhaustive work of Guye and Perrot \*, Kohlrausch †, and Lohnstein ‡, a determination of surface-tension in absolute measure by means of the drop-pipette can be obtained as follows:—

The expression giving the weight of a drop in terms of the tension is

$$g = r \alpha \Phi$$
,

where

 $\alpha$  = tension in millgrms./mm. g = weight of a drop in milligrams. r = radius of the orifice in mms.

 $\Phi$  is a function of  $\left(\frac{r}{a}\right)$ , where  $a^2$  is given by  $\frac{2\alpha}{\rho}$ ,

 $\rho$  being the density of the liquid in the pipette.

This applies to cases of liquid-gas tension, but it may perhaps be extended to the present case by taking into consideration the density of the medium in which the drop of oil is formed, *i.e.* the water.

Calling the density of the water  $\rho_w$ , we have

$$a^2 = \frac{2\alpha}{\rho_w - \rho_0}.$$

We have now to evaluate  $\Phi$ . The ordinary method of using the Lohnstein-Kohlrausch formula is to take some approximate value for  $\alpha$ ; from this calculate a, and hence  $\left(\frac{r}{a}\right)$ . Kohlrausch  $\S$  has given a table showing the values of  $\Phi$  for different values of  $\left(\frac{r}{a}\right)$  and by inter- or extrapolation  $\Phi$  can be evaluated. We then compare the value of g given by the expression  $r\alpha\Phi$  with g actually obtained by experiment; and finally, by a series of approximations,

<sup>\*</sup> Guye & Perrot, Archives d. Sc. Phys. 4th ser. vol. xi. p. 225 (1901); vol. xv. p. 132 (1903).

<sup>†</sup> Kohlrausch, Ann. d. Physik, vol. xx. p. 798; vol. xxii. p. 191 (1906). † Lohnstein, Ann. d. Physik, vol. xx. pp. 237, 606; vol. xxi. p. 1030 (1906).

<sup>§</sup> Kohlrausch, loc. cit. p. 805.

a is given such a value as to make the calculated and observed values of g identical.

Now a determination by Pockels \* gives the value 48.3 dynes as the tension between water "and a petroleum oil."

Assume in the present case

$$\alpha$$
=48 dynes per cm.  
=4.89 milligrams per mm.  
 $a^2$ =97.8;

Then

$$a = 9.8$$
,  
 $a = 9.8$ ,  
 $r = 1.5$ .

Hence 
$$\left(\frac{r}{a}\right) = 0.152$$
.

Unfortunately this value of  $\left(\frac{r}{a}\right)$  is a little beyond the lower limit of Kohlrausch's table, viz.:-

<u>r</u>	Φ.
0.300	4.45
0.5288	4.48
0.200	4.66

For  $\binom{r}{a} = .152$ , the value of  $\Phi$  by inspection of these numbers (assuming the values do not change in direction down to  $\left(\frac{r}{a}\right) = 152$  would be

g = 34.62 milligrms.

Now g found experimentally = 35.00 milligrms.

The value for the interfacial tension was therefore taken to be 48 dynes per cm. To distinguish this oil from another hydrocarbon oil which was found to have a tension of 33.6 dynes, they will be throughout designated oils "A" and "B," viz. :-

\* A. Pockels, Wied. Ann. lxvii. p. 668 (1899).

Phil, Mag. S. 6. Vol. 15. No. 88. April 1908.

<sup>†</sup> Note.—It may be as well to state here that although oil A was as carefully tested as oil B, the writer would lay greater stress on the accuracy of the determinations made with oil B.

Variation of the Interfacial Tension with the Concentration of Sodium Glycocholate Solutions.

## FIRST SERIES.—OIL A.

Aqueous solutions of the sodium glycocholate were prepared of the following concentrations:—

On being freshly prepared, the aqueous solutions of these concentrations were quite transparent, but with considerable rapidity—2 to 3 hours—in the case of the more dilute, a white turbidity manifested itself. All tension measurements were therefore made with fresh transparent solutions so that

the values obtained might be quite comparable.

The following table gives the results obtained with oil A. The first column gives the concentration of the solution; the second, the corresponding drop-number; the third gives the relative tension as deduced from the relation already obtained (pp. 507, 508), viz., that the drop-numbers are inversely as the tension; the fourth column gives the absolute values of the tension based on the oil-water determination 33.6 dynes/cm. and by applying the values of column 3.

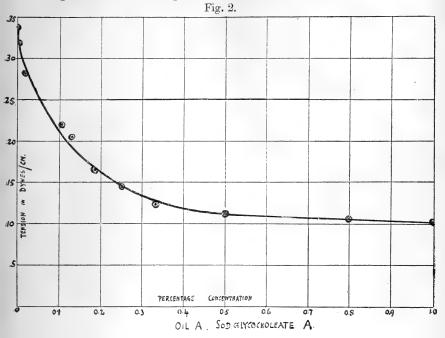
TABLE II.—Oil A.

Per cent. Concentration.	Drop- number.	Relative Tension.	Tension dynes/cm.
0	183	1.000	33.60
0.001	191	0.958	32.20
0.01	219	0.836	18 08
0.05	244	0.750	25.21
0.1	280	0.654	21.96
0.125	297	0.616	20.70
0.18	365	0.501	16.81
0.25	418	0.438	14.71
0.33	489	0.374	12.57
0.5	536	0.341	11.48
0.8	558	0.328	11.03
1.0	566	0.323	10.86

The above values in columns one and four are plotted in fig. 2. It will be noticed how exceedingly marked is the lowering effect of the sodium glycocholate upon the interfacial tension.

We are therefore, now, in a position to obtain an experi-

mental value for  $\frac{d\sigma}{dc}$  by simply taking the value of the tangent to the curve fig. 2 at the desired concentration.



SECOND SERIES .- OIL B.

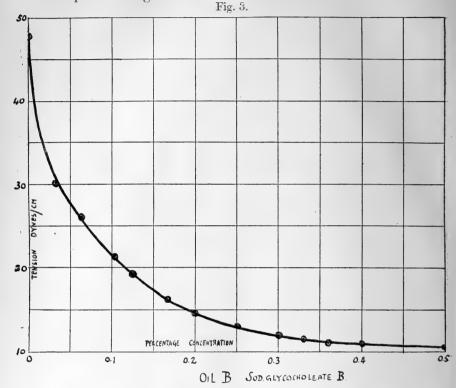
A similar series of determinations with oil B are given in the following table:—

TABLE III.—Oil B.

Per cent. Concentration.	Drop- number.	Relative Tension.	Tension dynes/cm
	100	1.000	40
U	128	1.000	48
0.0312	202	0.633	30.38
0.0625	233	0.549	26.35
0.125	317	0.404	19.39
0.165	375	0.341	16.37
0.200	417	0.307	14.73
0.250	471	0.272	13.05
0.300	522	0.245	11.76
0.330	531	0.241	11.57
0.360	557	0.230	11.04
0.400	568	0.225	10.80
0.500	585	0.219	10.51

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The above absolute values of Tension and Concentration are plotted in fig. 3.



In order to ascertain how far the values for the Tension obtained directly from the drop-number (column 4, Table III.) agreed with those obtained by applying Kohlrausch's formula

$$g = r \alpha \Phi$$

in each case, a comparison is made of the weights of the respective drops, using the values of the tensions for the two concentrations '25 per cent. and '5 per cent.

Per cent. Concentration.		of drop raΦ.	Weight of drop actually found.	
zero, i.e. distilled water	34·62 m	illigrms.	35 milligrms.	
·25 per cent.	8.89	29	8.60 ,,	
*5 ,,	7.01	,,	6.93 ,,	

Having in the foregoing obtained data for the experimental determination of the coefficient  $\frac{d\sigma}{dc}$  in the case of two different oils, the next procedure was to determine the value of  $\Gamma$ , *i. e.* the mass adsorbed per cm.<sup>2</sup> of oil-surface in excess of that which would have been there had no adsorption taken place at all. To express this quantity  $\Gamma$  more briefly, the term "Adsorption Coefficient," following the nomenclature of Ostwald, has been employed.

# Measurement of the Adsorption Coefficient.

Although the Adsorption Coefficient is defined as the excess mass of solute adsorbed, yet since the normal amount of solute per square cm. surface (when no adsorption has taken place) is very small in the present instance, this normal amount may be neglected in comparison to the total amount adsorbed per square cm. This is justifiable, as is evident from the following figures from an experiment detailed later:—

The bulk concentration of the glycocholate solution

= 25 per cent. or 0025 grams per c.c.

Assuming the thickness of the surface layer to be of the order of the range of molecular attraction, namely,  $13.4 \times 10^{-6}$  cms. (according to Parks\*), while the quantity adsorbed per cm.<sup>2</sup> in this particular case is  $5.4 \times 10^{-6}$  gram, the layer evidently possesses a concentration of 403 gram per c.c. The *surface* concentration is therefore about 160 times the *bulk* concentration.

It has been assumed that the thickness of the layer is of the dimensions of the range of molecular action. Of course the actual case is that there is a gradual "shading off" of the excess from the surface into the bulk of the solution, but practically all the excess is in the molecular surface-layer. This follows from the fact that the magnitude of the adsorption depends on the surface-tension, which is a phenomenon whose effects do not extend beyond the range of molecular attraction. As Gibbs † says:—"It is only within very small distances of such a surface that any mass is sensibly affected by its vicinity—a natural consequence of the exceedingly small sphere of sensible molecular action."

The experimental determination of the adsorption coefficient of sod. glycocholate at the surface of a hydrocarbon

<sup>\*</sup> Parks, Phil. Mag. [6] vol. v. p. 517 (1903). † Gibbs, 'Scientific Papers,' vol. i. p. 219.

oil was carried out, employing two distinct methods according as the adsorption took place under one of the two following conditions:—

(1) Adsorption at a very curved surface.

(2) Adsorption at an approximately plane surface.

# (1) Adsorption at a very curved surface.

A certain volume of sod. glycocholate solution of known strength is shaken (by a motor-driven shaker) for several hours, with a known volume of oil so as to form a uniform emulsion. The bulk concentration of the solution after emulsification is estimated, and the fall in concentration gives the total quantity of glycocholate adsorbed. To measure the adsorbing area, the droplets of the emulsion are examined under a microscope having a scale of known value in the eyepiece, and the average diameter of a droplet taken. Hence we obtain the radius r and the volume of a droplet  $-\frac{4}{3}\pi r^3$ . Knowing the total volume of oil emulsified, we obtain the total number of droplets \*, and since each drop has a surface area  $4\pi r^2$ , we finally obtain the total adsorbing area. Dividing the total quantity adsorbed by this area, the adsorption coefficient is determined.

The following are typical examples:—

## Determination with Oil A.

One litre of sod. glycocholate solution approximately '33 per cent. was made up, and of this 500 c.c. were shaken with '447 c.c. oil for 12 hours and allowed to stand 18 hours. The volume of oil was obtained by weighings—the density of the oil being '907. A drop of the emulsion was examined under the microscope.

Average radius of a droplet = 0000425 cm.

Hence surface area of one droplet= $4 \times 3.1416 \times (.0000425)^2$ .

and volume of one droplet =  $\frac{4}{3} \times 3.1416 \times (.0000425)^3$ .

Total volume of oil emulsified = 447 c.c.

- ... Total number of drops formed =  $1.3 \times 10^{12}$ .
- ... Total adsorbing surface  $= 31,553 \text{ cm.}^2$

To estimate the quantity adsorbed:—

A drop-number was taken with the pipette through a portion of the original solution. Drop-number=483, corresponding to a tension 12.80 dynes, which on fig. 2 indicates

\* Assuming that the density of an oil-droplet in the emulsion will sensibly coincide with the density of the oil in bulk.

a concentration 0.318 per cent. After adsorption had occurred, a drop-number through the emulsion gave 459 corresponding to a tension 13.44 dynes, which again corresponds on fig. 2 to a concentration .295 per cent.

## :. Fall in concentration = 023 per cent.

This was the general method adopted to determine change in concentration, it being much more delicate than any purely chemical means. It will be noticed that in the above the assumption is made that the emulsion particles themselves would not affect the value given by the pipette for the tension of the solution in which the emulsion is suspended. Justification of this is afforded by the concordance between the results obtained for the adsorption by this method and by an entirely different method to be described later. Continuing:—

Fall in concentration of .023 per cent. = .115 gram for the 500 c.c. solution employed.

Hence the mass adsorbed per cm.2, i. e.

$$\Gamma = \frac{\cdot 115}{31,553}$$

 $\Gamma = 3.6 \times 10^{-6}$  gram.

Similar determination of  $\Gamma$ , using Oil B :=

The solution made up gave a drop-number 531, corresponding on fig. 3 to concentration 317 per cent. 250 c.c. of solution were emulsified with 160 c.c. oil (density 900), and after emulsification the drop-number was 507, corresponding on fig. 3 to a concentration 290 per cent.

Hence the fall in concentration .....= 027 p. cent.

... Total mass adsorbed from the 250 c.c. soln. = :067 gram.

Total adsorbing area .....=11058 cm.<sup>2</sup>

∴ 
$$\Gamma = 5.9 \times 10^{-6}$$
 gram per cm.<sup>2</sup>

A further determination with a solution whose original concentration was 2 per cent. gave a value for the adsorption coefficient

$$\Gamma = 4.7 \times 10^{-6}$$
 gram per cm.<sup>2</sup>

An estimation of the probable error of these values really depends on the estimation of the radius of the emulsion particle. As great care as possible was taken to obtain

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these very uniform in size. The radius of a drop is taken as being 0000425 cm. The maximum value would be represented by

$$r = .00005$$
 cm.,

and as a minimum,

$$r = .000035$$
 cm.

Substituting these values in the first determination with oil B, we obtain the following result:—

$$\begin{array}{lll} r = \cdot 000035 & \text{cm.,} & \Gamma = 4 \cdot 4 \times 10^{-6} & \text{grm. per cm.}^2 \\ r = \cdot 000050 & , & \Gamma = 6 \cdot 9 \times 10^{-6} & , & , \\ r = \cdot 0000425 & , & \Gamma = 5 \cdot 9 \times 10^{-6} & , & , \end{array}$$

It is evident from these figures that the method is not sufficiently accurate to detect a different value of  $\Gamma$  corresponding to solutions of strengths '317 and '2 per cent. respectively. The different values obtained are within the limits of experimental error.

Comparison of Experimental values of  $\Gamma$  with Calculated values.

The calculated value for  $\Gamma$  is, as already pointed out,

$$-\frac{c}{\mathrm{RT}}\frac{d\sigma}{dc}$$
.

Let us take as a example the second determination with oil B:—

The concentration of the solution  $= c = \cdot 2$  per cent. =  $\cdot 002$  grm. per c. c.

Temperature T=289 abs.

R is the gas constant. For one gram of solute,

$$R = \frac{2 \times 4.2 \times 10^7 \text{ ergs}}{\text{molecular weight}}.$$

The molecular weight determined as already described is 140 in aqueous solution.

The coefficient  $\frac{d\sigma}{dc}$ , read from the curve fig. 3 at the point where c=2 per cent., gave

$$\frac{d\sigma}{dc} = \frac{9.5 \text{ dynes}}{.002 \text{ grm. per c. c.}} = 4750.$$

The true value of this probably lies between the limits 4800-4700, i. e., an error of about 2 per cent.

Hence

Fig. 4.

C

В

$$\begin{split} -\frac{c}{\text{RT}} \frac{d\sigma}{dc} &= \frac{.002 \times 4750 \times 140}{2 \times 4 \cdot 2 \times 10^{7} \times 289} \\ &= \frac{5 \cdot 5 \times 10^{-8}}{2 \times 10^{-6}} \text{ grm. per cm.}^{2} \\ \Gamma \text{ (found)} &= \frac{4 \cdot 7 \times 10^{-6}}{2 \times 10^{-6}} \text{ grm. per cm.}^{2} \end{split}$$

That is to say, the actual quantity adsorbed is about 85 times the calculated amount. This is far beyond experimental error, and there can be no doubt that a real discrepancy does exist. To confirm this, however, a different method of experimentally determining  $\Gamma$  was resorted to in which emulsions were dispensed with, as it was thought possible that the radius of the drops might be too near the value for the range of molecular forces.

(2) Adsorption at an approximately plane surface.

In the previous emulsion method we have been dealing with tension and adsorption at very curved surfaces. Owing to the discrepancy obtained in the above method, it is necessary to carry out determinations at a practically plane surface—i. e., one of very small curvature in comparison with the curvature of the sphere of molecular action.

For this purpose the apparatus shown in fig. 4 was devised. It consists of a bulb A, of about 170 c.c. capacity, which is filled with This bulb is connected to a long vertical narrow tube ( $1\frac{1}{2}$  metres high), having a rubber joint and pinchcock near the base so as to regulate the flow of oil. The upwardly directed nozzle of this tube is inserted through a cork into a wider tube B (1 cm. radius), which contains the solution through which the oil rises in the form of large drops. The tube B becomes constricted near the top, and then opens into a large cup-like vessel C. The sod.-glycocholate solution (about 1 litre) is poured into B and C until the constricted end of B is about 3 cms. below the surface of the solution. The upwardly moving drops of oil adsorb on their surface some of the solute and carry it through the constriction, the drops eventually coalescing. The object of the constriction is to prevent the

sod. glycocholate, which has once more been partially returned to solution (by the coalescence), from being carried back

into the lower part of the tube. When A is empty, the tube B (which has a rubber joint near the top) is nipped at this point and the upper portion disconnected. The lower solution (which is 250 c.c. in volume) is run off from below, and a drop-number through it taken with the pipette. The fall in concentration is read off by means of fig. 3—or, rather, a somewhat enlarged form of fig. 3; the enlargement being necessary for accurate readings on account of the very small changes in concentration produced by this method, the fewer large drops offering a very much smaller surface than the emulsion particles.

Example: Oil B.

One litre of '25 per cent. sod. glycocholate was prepared. The solution was poured into B and C as described, and after the drops have been passing for about 2 hours the reservoir A was empty and the contents of tube B run off. Through this solution a drop-number gave 466, i. e., a tension of 13·2 dynes, corresponding on the curve to a concentration '243 per cent.

Hence the fall in concentration = .007 per cent.

... for 250 c.c. (the volume of B) the total quantity removed = 0175 grm.

The volume of the oil-reservoir = 168 c.c.

The time of formation of 50 drops was taken at the beginning, in the middle, and near the end of the experiment. It was found that the middle value was the mean of the beginning and end, viz. 50 drops in 40 seconds.

Total time of emptying A . . = 7940 secs.  $\therefore$  total number of drops . . = 9925. Hence volume of a drop . . = 0169 c.c.  $\therefore$  radius of a drop . . . = 160 cm. and hence total adsorbing area = 3192 cm.<sup>2</sup>

 $\therefore$  Adsorption coefficient =  $5.4 \times 10^{-6}$  gram per cm.<sup>2</sup>

A second determination was made in which three times the former quantity of oil was used, and hence a greater fall in concentration was observed, which is in favour of a more trustworthy result:—

Total volume of oil used . . = 504 c.c. Total time of dropping . . = 20520 sees. Total adsorbing area . . . = 7414 cm.<sup>2</sup> Total mass adsorbed . . . = 022 grm.

 $\therefore$  Adsorption coefficient =  $3.1 \times 10^{-6}$ .

It is worthy of note that these values are of quite the same order as those obtained at the very curved surface in the emulsion method.

The calculated amount for this particular concentration (0.25 per cent.) gave

$$\frac{c}{RT}\frac{d\sigma}{dc} = 3.6 \times 10^{-8}$$
 gram per square cm.

We therefore find in this case also, that the experimental value for  $\Gamma$  far exceeds the calculated value. Thus over 98 per cent. of the total observed effect is unaccounted for in the theoretical calculation.

This result is unexpected, especially when one remembers that in this latter method of determining  $\Gamma$  the condition of planeness of surface is fulfilled to a very high degree of approximation; for the drops at the surface of which adsorption took place were of practically the same diameter as those produced by the drop-pipette in carrying out the measurements of  $\frac{d\sigma}{dc}$ ; i. e., the drops are very large in comparison to the sphere of molecular action. One would have expected, therefore, that the calculated result (dependent as it is on the value of  $\frac{d\sigma}{dc}$ ) would be in good agreement with

the experimental value of  $\Gamma$ .

One point of considerable interest lies, however, in the good agreement observable in the experimental values of  $\Gamma$  obtained by the two methods. On the one hand it appears to point (at least as far as one may rely on the accuracy of the determinations of  $\Gamma$ ) to the fact that the tension even at very great curvatures does not differ appreciably from that at an approximately plane surface. On the other hand, since the portion of the adsorption which is unaccounted for is so much greater than the value required by theory, it is possible that even considerable variations in this latter would be undetected owing to the "swamping" effect of the excess values.

#### DISCUSSION OF RESULTS.

The net result of the foregoing experiments is to show that between observed and calculated values there is a very great discrepancy—the actual quantity adsorbed being about eighty times the calculated amount. The most obvious explanation lies in the existence of some assumption in the theory which has been overlooked in practice. The following are Gibbs's assumptions in the deduction of the equilibrium equation:—

(1) The adsorbing surface is plane.

(2) The solvent is to show no concentration at the interface.

(3) For the particular equation used in the present paper, there is supposed to be only one component capable of being adsorbed.

(4) This component and the solvent in which it is dissolved

are supposed to form a single phase.

(1) Planeness of the surface.—It may be readily assumed that adsorption measurements made at the surfaces of oildrops of sensible magnitude approximate exceedingly closely to those at a plane surface.

(2) Absence of surface-concentration of the solvent.—This was simply assumed to be the case, no means of testing its

validity having as yet suggested itself.

(3) Adsorption of a single component.—This follows from the general experimental conditions, the solute, the sodium glycocholate, being the only substance whose adsorption is measured.

(4) Adsorption from a monophase system.—This assumption is implied from the actual example of surface-concentration given by Gibbs as exemplifying his theory, viz.:—A mixture of mercury- and water-vapours meeting at a liquid mercury surface, the water being the component which suffers surface-concentration. Mixtures of vapours are essentially monophase systems; and the question is, are we dealing with a monophase system in the case of an aqueous solution of sod. glycocholate? The evidence given by its osmotic behaviour in raising the boiling-points of water and alcohol and lowering the freezing-point of water, is strongly in favour of its being a true electrolyte, and hence of its solution being a monophase system.

Temperature Effects accompanying Adsorption.

All attempts at a direct determination of heat evolution or adsorption at the oil surface were negative. It may be shown, however, indirectly that a small *evolution* of heat must occur, from the observed variation of the interfacial tension with temperature. Thus, with a solution of concentration 3 per cent. and oil B, the following results were obtained:—

Temperature.	Tension in dynes per en		
16° C.	11.76		
41° C.	12.96		
67° C.	14.4		

We have here the remarkable phenomenon of the tension increasing with the temperature. But in similar experiments, using water alone instead of solution, there was a marked fall in the tension, as was to be expected, viz.:—

Temperature.	Tension in dynes per cn	
16° C.	48	
41° C.	40.8	
67° C.	37.1	

The increase in tension with temperature in the case of the glycocholate solution is to be accounted for, therefore, by partial "desorption" having taken place; that is, an increase of temperature in the case of the glycocholate solution decreases the quantity adsorbed, and hence, in accordance with the principle of Le Chatelier, adsorption must be accompanied by heat evolution.

Further experimental determination may make it possible to calculate the quantity of heat (Q) evolved per gram-mol. adsorbed by applying the

equation

$$\frac{d \log K}{dt} = \frac{Q}{RT^2},$$

where K = ratio of concentration in surface layer to the bulk concentration.

#### IV. APPLICATION TO THE THEORY OF DYEING.

The various theories which have been advanced to account for the process of dyeing may be roughly divided into

- (1) Purely chemical combination or solid solution.
- (2) Purely physical surface effects (i. e., Adsorption).
- (3) Partially surface effects and partially chemical combination.

A great mass of evidence has been brought forward in support of these different views, but it is not proposed in this place to discuss them \*. Mention should be made, however, of the most recent contribution, namely that of Freundlich †, whose results point very strongly to the absence of chemical combination, but leave it an open question as to whether dyeing is an example of adsorption in the sense of Gibbs's theory.

It is evidently essential to this view that dye-stuffs in solution should possess the property of lowering the interfacial tension. This, of course, cannot be determined in

<sup>\*</sup> For an account of these various theories one may consult the work of W. P. Dreaper—'Chemistry and Physics of Dyeing' (1906).
† Freundlich, Zeitschr. Phys. Chem. vol. lix. p. 284 (1907).

Freundlich's experiments owing to the presence of the solid phase, but considerable support would be given to the adsorption theory of dyeing if it were shown that dye solutions actually did lower the tension at the interface between the solution and an inert liquid. This liquid must of course be such as to exclude both chemical combination and solution.

With this object further measurements were made with the hydrocarbon oil B already experimented with, which was

to function as the substance to be "dyed."

Aqueous solutions of various concentrations of the following dyes were prepared:—Congo red (sodium salt), methyl orange (sodium salt).

It is hardly to be expected that in any of these cases there would be solution in, or chemical combination with, the oil.

# Congo Red.

A preliminary trial with this substance showed that there was a distinct lowering of interfacial tension. The following table gives the results obtained for solutions of different concentrations.

TABLE IV.

Per cent. Concentration.	Drop- number.	Relative Tension.	Tension in dynes/cm.
0.0	128	-1:0	48.
0.02	140	0.914	43.87
0.05	148	0.865	41.52
0.1	165	0.775	37.20
0.12	165	0.775	37.20
0.2	165	0.775	37.20
0.25	165	0.775	37.20

The results of Table IV. are plotted in fig. 5 (lower curve).

It will be noticed that after the concentration has reached 0·1 per cent. there is no further effect on the tension. This probably represents the maximum true solubility of the dye; and the minimum value for the tension might possibly be made use of as a practical method of ascertaining the optimum concentration for the dye-bath.

From the lower curve (fig. 5) we obtain the value of the coefficient  $\frac{d\sigma}{dc}$ , for the curve itself is practically a straight line. We may proceed, therefore, to apply the adsorption

equation already obtained and calculate the adsorption coefficient  $(\Gamma)$ .

Thus, taking as an example the solution of concentration

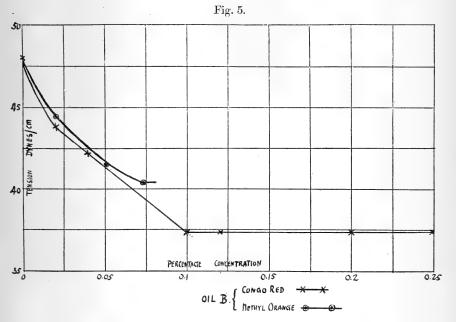
0.1 per cent.,

$$c = .001 \text{ grm. per c.c.},$$

$$\frac{d\sigma}{dc} = \frac{8 \text{ dynes}}{.001 \text{ grm./c.c.}}.$$

$$\therefore \frac{c}{\text{RT}} \frac{d\sigma}{dc} = \frac{\cdot 001 \times 8 \times 690}{289 \times 2 \times 4 \cdot 2 \times 10^7 \times \cdot 001} = \frac{2 \cdot 3 \times 10^{-7}}{289 \times 10^{-7}} \text{ gram per cm.}^2$$

where 690 = the molecular weight of the undissociated Congo red, assuming it to be a monosodium derivative. Of course there is doubt as regards the value, since we are dealing with the substance when dissolved.



Thus, assuming complete dissociation in solution, the value of the molecular weight would be 345, and the resulting value for the adsorption coefficient would be  $1.15 \times 10^{-7}$  grm. per cm.<sup>2</sup> On the other hand, if the dye is colloidal the molecular weight might possibly be much higher; though the behaviour of sod. glycocholate, by analogy, is rather against this.

Experimental result:-

250 c.c. of 0·1 per cent. Congo-red solution were shaken for fifteen hours with ·175 c.c. of oil. The resulting emulsion particles were examined under the microscope. It was found that  $r = \cdot 0000435$  cm.

Hence, calculating exactly as in the sod. glycocholate solutions, we obtain the Total adsorbing area =  $\frac{3 \times 175}{.000435}$  cm.<sup>2</sup>

The quantity adsorbed was determined as usual by taking a drop-number with the pipette through the emulsion. The drop-number was found to be 158, = that is, a tension 38.73 dynes/cm., corresponding on fig. 5 to the concentration '082 per cent.

- ∴ Fall in concentration = .045 grm.
- .. Adsorption coefficient  $\Gamma = 3.7 \times 10^{-6}$  grm. per cm.<sup>2</sup>

It will be observed that this is very much the same value as was obtained in the case of the sod. glycocholate, and shows a large discrepancy as regards the calculated value. The fact, however, of a lowered tension shows that adsorption effects in the sense of Gibbs's theory cannot be absent.

# Methyl Orange.

The solubility of this substance in water is small—a saturated solution being about 0.073 per cent. The following results were obtained:—

TABLE V.

Per cent. Concentration.	Drop- number.	Relative Tension.	Tension in dynes/cm.
0	128	1.0	48
0.018	138	927	44.49
0.036	143	-892	42.81
0.073	152	-842	40.41

These values are plotted in fig. 5 (upper curve).

It will be noted that fig. 5 has a marked difference in appearance to figs. 2 & 3. This is of course due to the solubility limit being reached in the former case before the tension has fallen much in value.

Experimental determination of  $\Gamma$ :—

250 c.c. of ·07 per cent. solution were shaken with oil and formed an emulsion.

The Fall in concentration = .032 per cent.

... Total mass adsorbed = '08 grm.

Adsorbing surface area  $=\frac{3 \times 204}{0000435}$  cm.<sup>2</sup>

 $\therefore$   $\Gamma$  =  $5 \cdot 5 \times 10^{-6}$  grm. per cm.²

Calculated value =  $1.2 \times 10^{-7}$  ,,

We have here a further repetition of the observed anomaly.

In considering the behaviour of these dyes in relation to the adsorption theory, it may be admitted that despite the discrepancy between the observed and calculated results, substantive dyeing, at any rate, must be more or less an adsorptive process. Possibly the actual mechanism of dyeing consists *first* in adsorption and *afterwards* coagulation possibly due to "colloidal neutralization." There may finally be some degree of chemical combination, which varies from case to case.

#### Note on Rosaniline hydrochloride and Crystal Violet.

A saturated aqueous solution of Rosaniline hydrochloride (about '06 per cent.) gave a drop-number of 140-i.e., a Tension of 43.87 dynes/cm. The decrease in interfacial tension is less marked than in methyl orange or Congo red. No further experiments were carried out with this substance. Also Crystal Violet dye concentration 1 per cent. gave a drop-number 230, and hence also shows a lowering of tension.

#### V. SUMMARY.

1. The object of the investigation has been to examine from an experimental standpoint Gibbs's theory of surface-concentration, as the chief cause of the phenomenon of Adsorption. By modifying Gibbs's fundamental expression for surface-concentration, an equation is obtained giving the mass of solute adsorbed per cm. in terms of the concentration of the solution and the change in tension at the interface, aqueous solution—hydrocarbon oil.

2. The material employed consisted of aqueous solutions of bile-salts, the solute being adsorbed at the hydrocarbon-oil surface. The mass adsorbed per cm.<sup>2</sup> oil surface was

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determined by two methods. The corresponding tension measurements were carried out by the drop-pipette method.

3. The results show a considerable discrepancy between the actual amount adsorbed and that calculated on Gibbs's theory—the actual amount measured being always in excess to the extent of twenty to eighty times the theoretical values.

4. Experiments with dye-stuffs show similar behaviour,

the discrepancy being of the order stated.

5. As regards the discrepancy noted, no suggestion is as yet offered. Further experiments are in progress employing other electrolytes and non-electrolytes as material for measurements of a similar nature.

In conclusion, I would express my indebtedness to Professor Donnan for his advice and criticism during the course of this work.

XLVIII. The Thermodynamic Corrections of the Nitrogen Scale. By Edgar Buckingham\*.

#### [Plates XV.-XVII.]

#### Introduction.

Let  $C_p$  be the specific heat at constant pressure expressed in ergs. Let v be the specific volume of the gas. Let  $\theta$  be the absolute thermodynamic temperature. Then the fundamental equation of the porous-plug experiment  $\theta$  be written:

$$\theta \left( \frac{\partial v}{\partial \theta} \right)_p = v + \mu C_p. \qquad (1)$$

This may easily be put into the form

$$\frac{v}{\theta} - \frac{v_0}{\theta_0} = \int_{\theta_0}^{\theta} \frac{\mu C_p d\theta}{\theta^2}. \quad (p = \pi = \text{const.}) \quad . \quad . \quad (2)$$

<sup>\*</sup> Communicated by the Author.

The absolute temperature by the constant-pressure scale satisfies the equation of definition

$$\frac{\mathbf{T}}{\mathbf{T}_0} = \frac{\mathbf{v}}{\mathbf{v}_0} \quad (p = \pi) \; ; \; \dots \; . \qquad (3)$$

whence by eliminating v from equation (2) we have

$$\frac{\mathbf{T}}{\mathbf{T}_0} - \frac{\theta}{\theta_0} = \frac{\theta}{v_0} \int_{\theta_0}^{\theta} \frac{\mu \mathbf{C}_p d\theta}{\theta^2}.$$
 (4)

Let  $T_0$ ,  $\theta_0$ ,  $v_0$  refer to the ice-point.  $T_0$  is then the reciprocal of  $\alpha$ , the mean coefficient of expansion of the gas at the constant pressure  $\pi$  between the ice and steam points;  $\theta_0$  is the absolute thermodynamic temperature of the ice-point;  $v_0$  is the specific volume at the ice-point under the pressure  $\pi$ . Equation (4) may be used to find the value T, on the absolute constant-pressure scale, of any temperature of which the value is  $\theta$  on the absolute thermodynamic scale. As a preliminary to this, the value of  $\theta_0$  must be found by successive approximations setting  $T=T_0+100$ ,  $\theta=\theta_0+100$ , and, to start with,  $\theta_0=273$ .

To perform the necessary integration, the value of  $\mu C_p$  must be known as a function of  $\theta$ . The value of  $\theta$  is very approximately 273+t, where t is the centigrade temperature by any of the common scales. Hence, since the second member of (4) is merely a small correction-term, it is sufficient if we can express  $\mu C_p$  as a function of 273+t, which will be denoted by  $\tau$ . In other words, if we can find the form of the equation  $\mu C_p = f(\tau)$ , we may write  $\mu C_p = f(\theta)$  in integrating equation (4).

# 2. Use of the Law of Corresponding States.

Our experimental knowledge of the value of  $\mu$  for any one gas is not sufficient to enable us to decide upon an equation  $\mu C_p = f(\tau)$  which shall inspire any confidence as a basis for extrapolation outside the small range of temperature within which the experiments have been made. We therefore have recourse to the law of corresponding states, and thus bring all the experiments on the various gases into one connected series.

We have to consider experiments on carbonic acid, oxygen, air, nitrogen, and hydrogen. We assume that for these gases there exists a single reduced equation of state,

$$F\left(\frac{p}{p_o}, \frac{v}{v_c}, \frac{\tau}{\tau_c}\right) = 0, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where  $p_c$ ,  $v_c$ ,  $\tau_c$  are the critical constants. This assumption 2 N 2

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is plausible for the diatomic gases and air, while we know by experiment \* that the isothermals of air and carbonic acid are congruent when drawn to the proper scales. Admitting this assumption, we conclude that in corresponding states, the reduced value of  $\mu C_p$  per gram-molecule, or

$$y = \frac{\mathrm{M}p_c}{\tau_c} \cdot \mu \mathrm{C}_p, \qquad (6)$$

is the same for all the gases, M being the molecular weight. But since the value of  $\mu$  is, for such pressures as are used in gas-thermometry, independent of the pressure, and therefore, at any given temperature, independent of the volume, we may, in considering the Joule-Thomson effect, regard two gases as being in corresponding states if only they are at corresponding temperatures. It follows that there must be a single equation,

$$\frac{\mathrm{M}p_c}{\tau_c} \cdot \mu \mathrm{C}_p = \phi \left( \frac{\tau}{\tau_c} \right) . \qquad (7)$$

or

$$y = \phi(\tau'), \quad \dots \quad \dots \quad (8)$$

which is satisfied by the experimental values for all the gases. To discover the form of this general reduced equation for  $\mu C_p$ , we plot the value of y as ordinate against the reduced temperature  $\tau'$  as abscissa; draw a smooth curve to represent the distribution of the points as nearly as possible; decide by inspection upon the general type of equation to be adopted; and, finally, adjust the constants by trial. If our use of the law of corresponding states is permissible, the points should all lie close to a single smooth curve; if they do not, the assumptions are faulty or the experimental data erroneous.

A similar process may be pursued with  $\mu$  alone, instead of  $\mu C_v$ . We may plot the values of

$$\mu' = \frac{p_c}{\tau_c} \mu \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (9)$$

against  $\tau'$ , and attempt to determine a curve

$$\mu' = \psi(\tau')$$
. . . . (10)

Since we know that we are dealing with approximations and that the reasoning is not rigorous, the justification of our procedure depends in either case upon its success.

<sup>\*</sup> Amagat, Journ. Phys. (3) vi. p. 5 (1897).

#### 3. Numerical Data.

We have now to consider numerical values. In Table I. are given the values of  $p_c$ ,  $\tau_c$ ,  $C_p$ , and M. The specific heats are assumed to be constant from  $0^{\circ}$  to  $100^{\circ}$  except for carbonic acid. The value for nitrogen is from Holborn & Austin\*, the others from Lussana†. For carbonic acid Lussana's mean value for a pressure of 1 metre of mercury is used as a basis, and the variation with temperature, assumed to be linear, is taken from the mean of the results of Regnault, E. Wiedemann, and Holborn & Austin. the values refer to a pressure of 1 metre of mercury.

TABLE I. Critical Constants, Specific Heats, and Molecular Weights.

Gas.	$p_c$ . (atmospheres).	$ au_{c}$ . $(=273+t_{c})$ .	$C_p \times 10^6$ . (ergs).	M. (mol. wt.).
CO <sub>2</sub>	72.9	304.4	7.90 (1 + 0.00107 t)	44
O <sub>2</sub>	50.8	154.2	9.37	32
Air	39.3	133	9.91	28.8
N <sub>2</sub>	33.6	128	9.87	28
$\mathbf{H}_2 \dots$	13 (19·4)	32	142:2	2

The data available on the cooling effect,  $\mu$ , are those of Joule and Kelvin ton all five gases; of Natanson & and of Kester | on carbonic acid; and of Olszewski I on the inversion-point for hydrogen. Of Joule and Kelvin's seventeen experiments on hydrogen, only those have been considered in which the impurity of the gas was small (Nos. 3, 5, 6, 7, 9, 13, 14, 15, 16, 17), the correction for impurity being very large and uncertain. The data for plotting the experimental curve  $y = f(\tau')$  are collected in

<sup>\*</sup> Phys. Rev. xxi. p. 260 (1905).

<sup>†</sup> Nuovo Cimento (3) xxxvi. p. 134 (1894). ‡ Kelvin, Math. and Phys. Papers, i. pp. 418-429. § Wied. Ann. xxxi. p. 502 (1888). | Phys. Rev. xxi. p. 260 (1905).

<sup>¶</sup> Phil. Mag. [6] iii. p. 535 (1902).

Table II. Column 1 gives the initials of the observers to whom the observations on  $\mu$  are due; column 2, the symbol of the gas; column 3, the reduced temperature of experiment; column 4, the value of  $\frac{Mp_c}{\tau_c} \cdot \mu C_p$  deduced from the observed value of  $\mu$ ; column 5, the number of separate experimental values of which  $\mu$  is the mean; column 6, the average amount of impurity in the gas; column 7, the value of y computed by equation (11); column 8, the differences  $y-y_{\rm calc}$ . The values given by Kester are extrapolated to zero impurity from experiments with amounts of impurity up to 2.2 per cent.

The points in Plate XV. represent the values given in columns 3 and 4 of Table II. They do all lie close to one smooth curve, including Olszewski's inversion-point \*. The curve drawn is a satisfactory representation of the experimental results; it is an equilateral hyperbola with the

equation

$$\frac{Mp_c}{\tau_c} \cdot \mu C_p = \frac{53}{\tau' - 0.5} - 10.$$
 (11)

It will be found upon examination that the points which, from the number of separate experiments involved and the purity of the gas, appear a priori to deserve the most confidence, lie on the whole closest to the curve.

Equation (11) is an empirical equation with three constants. It is therefore natural that it may be fitted to the observations somewhat more closely than one with only two constants: for example, the equation given by Rose-Innes†,

$$\mu = \frac{A}{\tau} - B, \quad \dots \quad (12)$$

which follows, for low pressures, from van der Waals's equation of state, or the reduced equation

$$\mu C_p = \frac{A}{\theta^2} - B, \quad . \quad . \quad . \quad (13)$$

deduced by D. Berthelot; from his form of the equation of state. But aside from the fact that there is one more arbitrary constant available, equation (11) has an advantage over the two just mentioned, in that it does not make the curve asymptotic to the vertical axis. Inspection of

<sup>\*</sup> Compare A. W. Porter, Phil. Mag. [6] xi. p. 554 (1906).

<sup>†</sup> Phil. Mag. [5] xlv. p. 227 (1898). ‡ Trav. et Mém. Bur. Int. xiii. (1903).

TABLE I
II.—Reduced
Cooling
Effect

O. J. and T	J. and T	J. and T	J. and T	K.  " " " N. J. and T.  " " " " " " " " " " " " " " " " " "	1. Observers.
H <sub>2</sub> .	" " "	Air.	O <sub>2</sub> ,	CO <sub>2</sub> ;	2. Gas.
6·02 8·74 11·39	2·189 2·847 2·852	2·106 2·350 2·750	1.827 2.351 2.390 1.827 2.359 2.359	0-896 0-964 1-027 1-027 1-1092 1-1158 1-214 0-963 0-921 1-010 1-074 1-204 1-217	$(=\tau/\tau_c).$
- + 0·0 - 3·36 - 5·04	22·1 12·3 16·4	21·9 18·7 12·7	31.2 23.4 16.6 31.9 16.9	118.5 103.4 8.8.9 8.8.9 77.5.0 99.3 108.3 87.1 58.4 88.4	$\left(=\frac{\mathbf{M}p_c}{\tau_c},\mu\mathbf{C}_p\right).$
51 th	<b>                                      </b>	တာတတ			5. Number of experiments.
4:5 4:5	7.9 2.2 12.5		51 51 546 5294	68.2 1.8.2 1.7	6. Average impurity (per cent.).
-0.40 -3.57 -5.11	21·4 12·6 12·5	23·0 18·6 13·6	29-9 18-6 18-0 29-9 18-5 18-1	123.8 104.2 90.8 79.5 70.5 115.9 115.9 93.9 93.9 65.3 65.3	7.  y <sub>calc.</sub> (by equ. 11).
+0.4 +0.21 +0.07	+0.7 -0.3 +3.9	$-1.1 \\ +0.1 \\ -0.9$			$8.$ $y-y_{\rm calc.}$

Plate XV. shows that the observations on carbonic acid indicate approach to an asymptote at about  $\tau'=0.4$  or  $\tau'=0.5$ . Repeated trials have shown that the observations cannot be so well represented by any simple curve asymptotic to the vertical axis. If such a curve be made to fit the carbonic acid points at all well, the agreement is spoiled for the important group of points between  $\tau'=2$  and  $\tau'=3$ , representing the observations on oxygen, air, and nitrogen.

Nearly as good an agreement may be obtained by the more elementary method of plotting  $\mu' = \frac{p_c}{\tau_c}$ .  $\mu$  against  $\tau'$ . This is done in Plate XVI. Curve  $\dot{A}$  has the equation

$$10^{9} \frac{p_{c}}{\tau_{c}} \cdot \mu = \frac{163.9}{\tau' - 0.42} - 2.36(\tau' - 0.42) - 15.9, \quad (14)$$

and is based on the assumption that the critical pressure of hydrogen is 19.4 atmospheres. Curve B, with the equation

$$10^{9} \frac{p_{c}}{\tau_{c}} \cdot \mu = \frac{206 \cdot 7}{\tau' - 0.32} - 36.3, \quad . \quad . \quad (15)$$

assumes that  $p_c = 13$  atmospheres for hydrogen. Slight changes may, of course, be made in the constants of equations (11), (14), and (15), but no great improvement is possible.

## 4. Integration of the Constant-Pressure Equation.

The various detached observations on the Joule-Thomson effect may thus be coordinated and made to support one another. It seems probable that any one of the three empirical equations, (11), (14), and (15), gives the true values quite as closely as the observations on any one gas separately, except perhaps in the case of carbonic acid. Moreover, the existence of a general curve which represents the observations affords a very plausible means of computing the values of  $\mu$  or of  $\mu$ C<sub>p</sub> for any one gas all the way from its critical temperature to some twelve times its critical temperature.

Let us, for the present, confine our attention to equation (11). From this we may evidently obtain an unreduced equation of the form

$$\mu C_p = \frac{a}{\tau - b} - c \quad . \quad . \quad . \quad (16)$$

for each gas. If we now integrate equation (4) on the assumption that  $\mu C_p$  is correctly represented by equation (16)

and identify  $\tau$  with  $\theta$ , we get

$$\frac{\mathbf{T}}{\mathbf{T}_0} - \frac{\theta}{\theta_0} = \theta \left\{ \mathbf{A} \left( \frac{1}{\theta} - \frac{1}{\theta_0} \right) + \mathbf{B} \log_{\theta} \frac{\theta_0(\theta - b)}{\theta(\theta_0 - b)} \right\} . \quad (17)$$

where

$$A = \frac{1}{v_0} \left( \frac{a}{b} + c \right)$$

$$B = \frac{1}{v_0} \left( \frac{a}{b^2} \right)$$
(18)

In Table III. are given numerical values of the constants for use in computing, including the values of  $\theta_0$  found by carrying on the successive approximations until the last two values of  $\theta_0$  differed by less than 0°·001. The values of the coefficient of expansion  $\alpha$  are from Chappuis's\* determinations. The figures given for each gas form a consistent system of values which may be substituted in equation (17) for finding the relation of the constant-pressure scale of that gas to the thermodynamic scale. After finding the value T corresponding to a given value of  $\theta$ , we form the differences  $\theta - \theta_0$  and  $T - T_0$ . The quantity  $\theta - \theta_0$  is the centigrade thermodynamic temperature  $t_\theta$ , while  $T - T_0$  is the centigrade constant-pressure temperature  $t_p$ . The "scale correction," or the amount by which the temperature on the constant-pressure scale lags behind that on the thermodynamic scale when both are made to agree at 0° and 100°, is then simply  $t_\theta - t_p$ .

Table III.

Data for computing the Constant-Pressure Scale-corrections.

	Air.	Nitrogen.	Hydrogen.	Carbonic Acid.
Pressure, π (mm.)	1001	1002	1000	998
ь	66.5	64	16	152.2
log <sub>10</sub> A	$\overline{2}$ 36589	$\overline{2}$ 41525	$\overline{2}$ ·22721	$\overline{2}$ ·45709
log <sub>10</sub> B	$\overline{4.50392}$	$\bar{4}$ ·56992	$\bar{4}$ .98394	$\overline{4}$ $\cdot 23553$
1+100 α	1.367282	1.367315	1:366004	1.374097
То	272-270	272.246	273-221	267:310
θ <sub>0</sub>	273.273	273:286	273.049	273-267

<sup>\*</sup> Trav. et Mém. Bur. Int. xiii. (1903).

Equations (14) and (15) may be treated in a similar way. For equation (15) the form of the integral, assuming  $C_p$  to be sensibly constant, is the same as for equation (11). For equation (14) it has one more term and is therefore slightly less convenient for computing. The values of the constants need not be given, as they follow from Table II. and equations (14) and (15).

## 5. Constant-Pressure Corrections for Nitrogen.

If the foregoing methods be used to compute the thermodynamic corrections of the constant-pressure hydrogen scale, the results do not agree, except qualitatively, with those of D. Berthelot\* and Callendar†. The two methods of computation used by Callendar also give very different results. All the computed corrections are small, and it seems probable that the true corrections are negligible except in work of the highest precision, but the absolute values cannot be determined with certainty from the data at present available.

In the case of nitrogen the state of affairs is more satisfactory. In Table IV. are collected the results of Rose-Innes‡, Callendar, Berthelot, and the writer for temperatures between the ice and steam points. The figures given by Rose-Innes and Callendar for atmospheric pressure have been multiplied by  $\frac{4}{3}$  to make them comparable with the others. The agreement of the four sets of corrections is satisfactory.

#### TABLE IV.

Thermodynamic corrections of the Constant-Pressure Nitrogen Scale between the ice and steam points, for  $\pi = 1000$  mm.

(The corrections are to be subtracted from the constant-pressure readings.)

t° C.	Rose-Innes (1901).	Callendar (1903).	Berthelot (1903).	Buckingham (1907).	Mean.
10 20 30 40 50 60	0·0288 0·0289 0·0269	0·0109 0·0188 0·0236 0·0260 0·0260 0·0240 0·0204	0·010 0·017 0·022 0·024 0·024 0·022 0·019	0·0078 0·0137 0·0179 0·0203 0·0209 0·0198 0·0172	0·010 0·017 0·022 0·025 0·025 0·023 0·020
80 90	0.0168	0·0151 0·0081	0·014 0·007	0·0129 0·0071	0·015 0·008

<sup>\*</sup> Trav. et Mém. Bur. Int. xiii. (1903).

<sup>†</sup> Phil. Mag. [6] v. p. 48 (1903). † Phil. Mag. [6] ii. p. 130 (1901).

The corrections at higher temperatures, where the hydrogen thermometer cannot be used, are of more interest. A comparison of these values is given in Table V., Callendar's values having been reduced to  $\pi = 1000$  mm. as before. The relation of the several sets of corrections may be seen from the curves in Plate XVII. Curve A represents Berthelot's values. Curve  $B_1$  represents the values computed by equation (14) with Holborn and Austin's values of  $C_p$ . Curve  $B_2$  represents the results obtained by means of equation (11). Curve C represents Callendar's results. The greatest discrepancy at  $1000^{\circ}$  is less than  $0^{\circ}$ ·4, an amount which is negligible in the present state of gas-thermometry.

Table V. Constant-Pressure corrections for Nitrogen at high temperatures.  $\pi$ =1000 mm.

(The corrections are to be added to the constant-pressure readings.)

1.	2.	3,	4.	5.	6.
t° C.	Callendar.	Berthelot.	Buckingham (equ. 11).	Buckingham (equ. 14).	Buckingham (equ. 15).
200 400	0.135	0·113 0·457	0·128 0·523	0·105 0·433	0.456
450 600	0.660	0.844	0.992	0.827	
800 1000 1200	2:047	1·248 1·654	1·492 2·007 2·532	1·262 1·706 2·157	1·721 2·170
1600	***	•••	3·596 4·672	2 101	2110
2000	***	•••	10/2		

The agreement of  $B_1$  with A and of  $B_2$  with C is so close as to suggest premeditation. In reality equation (14) was developed and the values represented by curve  $B_1$  computed before the writer had succeeded in obtaining a copy of M. Berthelot's paper. That paper then suggested further work which resulted in the development of equation (11) from which were computed the values represented by curve  $B_2$ . Equations (14) and (15) were deduced on the assumptions that the critical pressure of hydrogen was 19·4 atmospheres and 13 atmospheres, respectively. It is evident therefore, upon comparing columns 5 and 6 of Table V., that small errors in the critical constants, while they have some influence on the reduced equation for  $\mu$  or  $\mu C_p$ , are almost entirely eliminated in the process of finding the coefficients of the corresponding unreduced equation.

#### 6. Relation of the Constant-Pressure and Constant-Volume Scales.

It is impossible to treat the theory of the constant-volume thermometer by means of the Joule-Thomson effect, without making some assumption regarding the form of the equation of state for the low pressures concerned in gas-thermometry. But if the equation of state be known, the relation of the constant-pressure and constant-volume scales may be found directly. There is then no object in integrating the general equation of the constant-volume thermometer, for the thermodynamic corrections of the constant-volume scale may be found from those of the constant-pressure scale already computed.

Let us assume that the isothermal lines pv=f(p) are sensibly straight at low pressures, as experiment shows them to be for the more nearly ideal gases. Let the departures of the gas from Boyle's law at low pressures be represented

by the equation

$$p_2v_2=p_1v_1[1+K(p_2-p_1)], \dots (19)$$

in which K is small and nearly constant. Then if  $\alpha$  and  $\beta$  are the coefficients of expansion and of pressure, we may easily deduce the equation

$$t_p = \frac{\beta}{\alpha} \frac{1 - K\pi}{1 + K\beta\pi t_v} t_v, \qquad (20)$$

in which  $t_p$  and  $t_v$  are the numerical values of any given temperature on the centigrade constant-pressure and centigrade constant-volume scales, respectively, and  $\pi$ , the constant pressure in the one case, is the same as  $p_0$ , the initial pressure at the ice-point, in the other.

If we assume that the behaviour of the gas at low and moderate pressures is represented by the equation of Clausius,

$$\left[p + \frac{a}{\theta(v+c)^2}\right](v-b) = \mathbf{R}\theta, \quad . \quad . \quad . \quad (21)$$

we find that as the pressure approaches zero, the coefficient K of equation (19) approaches the limit

$$K = \frac{\theta_0}{\theta} \left( b - \frac{a}{R} \cdot \frac{1}{\theta^2} \right) \cdot \dots \quad (22)$$

The values of b and of  $\frac{a}{R}$  may be found from Chappuis's \*

<sup>\*</sup> Trav. et Mém. Bur. Int. xiii. (1903).

experiments on nitrogen, and the numerical equation is

$$K = \frac{\theta}{\theta_0} \left( 0.001410 - \frac{147.95}{\theta^2} \right)$$
 . (23)

The unit of pv is here taken to be the value that pv approaches at the ice point as the pressure approaches zero, and  $\theta_0$  is taken equal to 273.2.

#### 7. Constant-Volume Corrections for Nitrogen.

Equations (20) and (23) have been used to compute the difference of the two nitrogen scales and thence the thermodynamic corrections of the constant-volume scale. In this latter process the constant-pressure corrections given in Table V., column 5, were used. A comparison of results is given in Table VI. and, graphically, in Plate XVII. Curve A' represents Berthelot's values; curve  $B_1$ , those just computed; curve C', Callendar's values. If  $B_2$  had been used as a basis instead of  $B_1$ , we should have had another curve  $B_2$  lower than  $B_1$  by the same amount as  $B_2$  is lower than  $B_1$ .

TABLE VI.

Constant-Volume corrections for Nitrogen at high temperatures.  $p_0=1000$  mm.

(The corrections are to be added to the constant-volume readings.)

t° C.	Callendar.	Berthelot.	Buckingham (equ. 14).
200	0.035	0.046	0.024
400		0.194	0.139
450	0.189		
600	•••		0.305
800		0.56	0.514
1000	0.646	0.77	0.734
1200		* * *	0.961

We have thus, for each of the two nitrogen scales, the independent results of three writers using different methods of computation. The various values of the thermodynamic corrections show an agreement, for each scale, which is closer than has been attained in independent determinations of high temperatures with the gas thermometer, and it seems probable that the means of the values represented by curves A,  $B_{\rm l}$ , and C, or A',  $B_{\rm l}$ ' and C' of Plate XVII. give very nearly the true values of the corrections in question.

If the pressure in the thermometer, namely  $\pi$  or  $p_0$ , is less than 1000 mm., as it usually is in practice, the corrections are to be reduced in the same ratio. This process of reduction is not rigorous, but it is correct to a much higher degree of approximation than that to which the corrections for 1000 mm. are known.

National Bureau of Standards. Washington, D.C., November 9, 1907.

XLIX. On Anomalous Magnetic Rotatory Dispersion of Rare Earths. Remarks on Prof. R. W. Wood's recent paper. By G. J. Elias\*.

ROF. R. W. Wood having recently published an investigation on anomalous dispersion of magnetic rotation in neodymium, I should like to direct attention to expe-

riments which I made in 1906‡.

For measuring the rotation I used a Lippich polarimeter, illuminated by light having passed through a spectrometer, and monochromatic to within  $\frac{1}{2} \mu \mu$  about. The rotation varying very rapidly within the absorption-band and near its edges, a high degree of homogeneity of the light is necessary; otherwise it may occur that the most important points of the curve are overlooked, as I actually found. Of course through the light not being absolutely homogeneous small errors will come in; nevertheless it seems to me that this direct method should give much better results than that used by Prof. Wood, which I rejected on account of its inaccuracy and the errors occurring necessarily in the neighbourhood of absorption-bands. Moreover, I consider it impossible to make measurements within the absorption-band in that way; but this is most desirable in order to detect many peculiarities of the band's structure and to find the sense of rotation on both sides of the maximum.

In the case of the absorption-band of a solution of chloride of erbium, at about  $\lambda = 520 \mu\mu$ , to which I confined my first measurements, I found considerable anomalies, and the sense of rotation in the immediate neighbourhood of the maximum positive, farther away negative, as is shown by

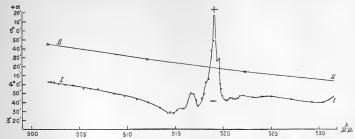
<sup>\*</sup> Communicated by Prof. H. du Bois.

<sup>†</sup> R. W. Wood, Phil. Mag. [6] xv. p. 270 (1908); also R. W. Wood, Physik. Zeitschr. vi. p. 416 (1905); ix. p. 148 (1908).

† G. J. Elias, Physik. Zeitschr. p. 931 (1906). See also H. du Bois

and G. J. Elias, Proc. Roy. Acad. Amsterdam, Feb. 29, 1908.

the annexed curves; for further details my paper may be referred to. From this fact I will not draw any further



I=Double magnetic rotation of the plane of polarization in a solution of chloride of erbium, ½ to ½ normal, in glass vessel. Field 7500 gauss.

II=The same for water, in the same vessel.

conclusions in this short notice. Of course the peculiar behaviour of the rotation will be closely connected with the very complicated structure of the band, not to be seen in the liquid solution, but very clearly in solid solutions, especially at

liquid air temperature \*.

I am busy continuing these investigations, as well as those on absorption, refraction, and related phenomena, with different salts of the rare earths, solid and dissolved, and am using for the purpose a monochromatic autocollimating illuminator, made by Zeiss in Jena, a description of which will shortly appear.

Berlin, Bosscha Laboratory, Feb. 15, 1908.

L. The Irregularities in the Radiation from Radioactive Bodies. By Hans Geiger, Ph.D., John Harling Fellow, University of Manchester †.

In all experiments in which the ionization currents due to two radioactive substances are balanced against each other by means of an electrometer, it is not found possible to obtain an exact balance. The needle of the electrometer always moves quite irregularly over a certain number of divisions on the scale. This effect cannot be eliminated, no matter how much care is taken in the adjustment. Bronson ‡, who was troubled by this effect in the use of his steady

<sup>\*</sup> H. du Beis & G. J. Elias, loc. cit.

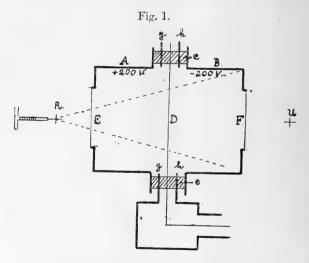
<sup>†</sup> Communicated by Professor E. Rutherford, F.R.S. † Bronson, Phil. Mag. Jan. 1906, p. 143.

deflexion electrometer, suggests that the effect may be due to an exceedingly small and rapid change in the ionization itself. E. v. Schweidler\* has in a special paper drawn attention to the fact, that according to the disintegration theory certain irregularities in the radiation from radioactive substances are to be expected. He calculates from the laws of probability that these irregularities should under certain conditions be within the limits of measurement. K. W. F. Kohlrausch† made some experiments to test the accuracy of the theory of v. Schweidler. A discussion of his results will be given later.

In the course of some experiments, my attention was attracted by the impossibility of obtaining a steady balance of two opposite ionization currents due to the  $\alpha$  rays. A few experiments will now be described which I have made to test

the cause and the magnitude of these irregularities.

It was of importance first to prove whether the effect was due to a real variation of the intensity of the radiation or to some secondary effect which might be eliminated. For this purpose, the following experiment was made:—Two ionization vessels, A and B, were arranged as shown in fig. 1. Between

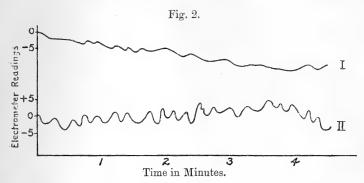


them, and insulated from them by the ebonite plugs e, c and the guard-rings g and h, was fixed a piece of aluminium foil D, which was connected with an electrometer of the Dolezalek

<sup>\*</sup> E. v. Schweidler, Congrès international pour l'étude de la radiologie et de l'ionisation, Liége 1905. † K. W. F. Kohlrausch, *Wien. Ber.* 1906, p. 673.

type. The vessels A and B were closed at E and F by aluminium foil and connected with the opposite poles of a battery of 400 volts, the middle point of which was earthed. A narrow pencil of  $\alpha$  rays was sent through both vessels from the point R, and as in practice the vessel B was somewhat larger than A it was easy to balance the two opposite ionization currents. Now in this case any effect of the irregularities of the radiation itself was eliminated, since each  $\alpha$  particle contributed equally to the ionization currents both in A and B.

The experiment, however, did not show an entire absence of the oscillations of the electrometer needle, but the effect was undoubtedly smaller than when the ionization currents of the same intensity were produced from two different sources at R and U, R producing ions only in A and U only in B. The two curves given in fig. 2 correspond to the movement

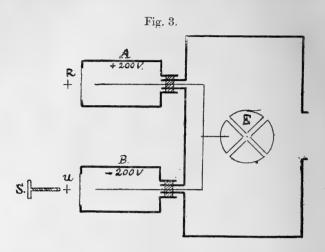


of the needle of the electrometer over a time of 4.5 minutes. Curve I. shows the effect due to one source of rays, Curve II. the effect of two separate sources. The intensity of the radiation was the same for both curves. The small oscillating effect shown in Curve I. was probably due to the irregular thickness of the aluminium foil D. Some of the particles were stopped in the leaf and could not produce ionization in B, while other particles passed through the small holes, thus producing a stronger ionization in B than in A.

The general arrangement used for the further experiments is shown in fig. 3. E is the electrometer of which one pair of quadrants was earthed and the other pair connected with two ionization vessels A and B. The outsides of the vessels were charged up to +200 and -200 volts respectively. The radiation from suitable radioactive substances was allowed to pass into the vessels through two openings which were covered with

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aluminium foil in order to avoid possible disturbances from air-currents. By means of a screw S the distance of the radioactive matter U from the vessel B could be varied and a balance obtained between the ionization currents in A and B. When the balance was obtained as closely as possible,



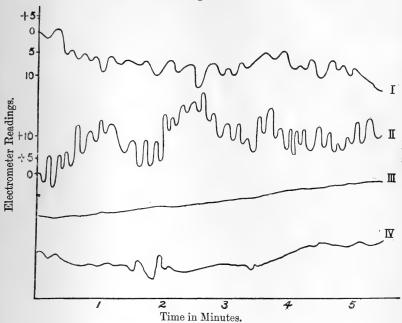
the needle of the electrometer showed small oscillations which were observed over a definite time, generally five minutes.

With this arrangement, a comparison was made between the irregularities of the ionization currents produced by  $\alpha$  particles with those produced by a current of the same intensity

due to  $\beta$  particles.

Two wires which had been exposed to the radium emanation were placed at R and U quite close up to the vessels A and B (fig. 3). The ionization in this case is almost entirely due to a particles. The oscillations of the needle over a space of five minutes are shown in the Curves I. and II. of fig. 4. The intensity of the radiation was for Curve I. 340 and for Curve II. 1100 divisions per minute on the electrometer-scale, where one division corresponds to the calculated ionization produced by about 22 a particles. The Curves III. and IV. of the same figure were obtained under the same conditions except that the ionization in the cylinders A and B was produced by  $\beta$  particles. For this purpose a little glass tube containing about 5 mg. RaBr<sub>2</sub> was brought near to the vessels and its distance adjusted till the ionization in both cylinders was equal and of the same intensity as in the case of the  $\alpha$  particles. The Curves III. and IV. correspond to I. and II. respectively as regards the intensity of the ionization currents. The Curve III. shows





no oscillations at all, while IV. shows oscillations but comparatively to a very slight extent. The fact that hardly any observable oscillations occurred in the case of  $\beta$  radiation shows, independently of any theory, that the effect observed with  $\alpha$  radiation is really due to the irregular nature of the  $\alpha$  radiation, and not to a secondary effect.

The difference in the shape of the curves is to be expected from simple theoretical considerations. It is known that the absolute average error in a large number of observations for two events P and Q is given by

$$\epsilon = \pm \sqrt{Npq}$$

where N is the number of observations and p and q are the probabilities for the events P and Q respectively. If we apply this formula to radioactive changes, taking N as the number of atoms present, the number of atoms breaking up during a given time  $\tau$  ( $\tau$  being small compared

with the period of the substance) is given by  $\lambda \tau N$ , the number of atoms still unchanged after the time  $\tau$  is given by  $(1-\lambda \tau)N$ . From this it follows that the probability of a single atom breaking up during the time  $\tau$  is  $\lambda \tau$ , while the probability that the same atom will exist after that time is  $1-\lambda \tau$ . Hence the absolute average error is

$$\epsilon = \pm \sqrt{N\lambda\tau(1-\lambda\tau)},$$

or, neglecting the square of  $\lambda \tau$  compared with  $\lambda \tau$  itself, the error is

$$\epsilon = \pm \sqrt{N\lambda\tau}$$
 or  $\pm \sqrt{Z}$ ,

where Z is the number of atoms disintegrating during the time  $\tau$ . This result was first deduced by E. v. Schweidler (loc. cit.) in a similar manner.

According to the simple radioactive theory, the average number of atoms breaking up during the time  $\tau$  is given by

$$Z = N\lambda \tau$$
.

The actual number observed may show a deviation from this, or an average error equal to the square root of the number of atoms breaking up during the time  $\tau$ . The absolute average error increases therefore with the number of atoms breaking up, *i.e.* with the intensity of the radiation;

while the relative error  $\frac{\sqrt{Z}}{Z}$  decreases. The movement of the needle of the electrometer registers the absolute error.

The correctness of this theoretical conclusion may be tested as follows:—Rutherford has shown that one  $\alpha$  particle from radium itself produces 80,000 ions in its path of 3.5 cms. in air at atmospheric pressure; while Durack has found that each of the swifter  $\beta$  particles from radium expelled at a speed approaching that of light makes a new pair of ions in every 6 cms. of air at 1 mm. pressure. Consequently, in the cylinders A and B which were about 12 cms. in length one  $\beta$  particle will produce at atmospheric pressure  $4 \times 760$  or about 3000 ions. Therefore, in order to produce the same ionization current with  $\beta$  particles, about 25 times as many  $\beta$  particles as  $\alpha$  particles are necessary. Hence the average error in the number of  $\beta$  particles shot out is

$$\epsilon = \pm \sqrt{25Z}$$
.

The average error measured by the electrometer is

$$\epsilon = \pm \frac{1}{25} \sqrt{25Z}$$

as one  $\beta$  particle produces only an effect  $\frac{1}{25}$  of that produced

by one  $\alpha$  particle. Therefore the error measured in the case of  $\beta$  particles, on the same electrometer and under the above-mentioned conditions, should be about one-fifth of that observed for  $\alpha$  particles giving the same intensity of ionization. The smallness of the irregularities in Curves III. and IV. (fig. 4) compared with those shown in Curves I. and II. is thus to be expected.

A special series of measurements has been made to show how the average error depends upon the intensity of the radiation. At the points R and U (fig. 3) two wires were placed which were made intensely active by exposure to the radium emanation. While the activity was decaying, the oscillations of the needle were observed at intervals, and curves were drawn showing the oscillations as accurately as possible over intervals of  $5\frac{1}{2}$  minutes. From these curves the average error was determined by counting the divisions passed over by the electrometer needle during the attempted balance, and dividing that number by the number of swings observed during the same time. The average error was also calculated theoretically. An example may be given.

#### Experimental Determination of the Error.

The data are taken from Curve II. (fig. 4). The number of divisions passed over in  $5\frac{1}{2}$  minutes, counting the maximum divergence both positive and negative, was 380 and the number of oscillations during that time was 64. Hence the average magnitude of one oscillation was  $\frac{380}{64} = 5.9$  divisions, and the average deviation or the error  $\pm 2.95$  divisions.

#### Theoretical Determination of the Error.

The error is given by  $\sqrt{Z}$  where Z is the number of atoms breaking up during the time  $\tau$ . This number gives also the number of  $\alpha$  particles shot into the vessel during the time  $\tau$ . The time  $\tau$  is in this case the average time of swing, being 5.8 sec. as an average taken from all the curves. The intensity of the radiation of one wire was 1100 divisions per minute, and therefore, as one division corresponds to the ionization produced by about 22  $\alpha$  particles, the number of particles shot into the vessel is  $2.4 \times 10^4$  per minute, and therefore the number shot into both vessels in 5.8 sec. is

$$2 \times 2.4 \times 10^4 \times \frac{5.8}{60} = 4.7 \times 10^3$$
.

The square root of this is 68. The average error taken over

5.8 sec. is thus  $\pm 68$   $\alpha$  particles or transformed into divisions  $=\pm \frac{68}{22} = \pm 3.1$  divisions.

The figures in the following table are all calculated in the same way as indicated in the above example. The difference between the theoretical and experimental error is about 15 per cent.

Absolute error determined.		
Theoretically.	Experimentally.	
6·4 div.	5.4 div.	
4.9 ,,	4.4 ,,	
3.1 ,,	2.9.,,	
2.1 ,,	2.1 ,,	
0.9 ,,	1.3 "	
	Theoretically.  6.4 div.  4.9 ,,  3.1 ,,	

The agreement is better than one would expect considering the conditions of the experiment and the uncertainty of the data from which the number of  $\alpha$  particles is deduced. A slight correction ought also to be made since the electrometer needle was not quite dead-beat. The agreement between theory and experiment is quite as close if the error is determined by measuring the magnitude of the oscillations of the electrometer-needle for any convenient time, for example, each half minute, instead of the time of swing of the electrometer, viz. 5.8 seconds.

Kohlrausch (loc. cit.) did not find a numerical agreement between the theory and his experiments, but this seems to be due to an incorrect use of the formula, since on calculating the error as above from his data, quite a close agreement (10 per cent.) is obtained for saturation currents. If the current is not saturated, as was the case in some of Kohlrausch's experiments, the above formula cannot be applied. For if the current is only half saturated, half of the ions produced from each  $\alpha$  particle are lost by recombination; consequently each  $\alpha$  particle produces only one half of its effect under ordinary conditions of saturation. Taking this fact into consideration, a close agreement between theory and experiment was also found by calculating the data given by Kohlrausch for non-saturated currents.

The agreement between theory and experiment in Kohlrausch's paper seems to me to be of special interest, for the method used by him differs from the method employed in this paper, while the intensity of the radiation in his experiments was nearly twenty times greater than the strongest used in mine.

I have to thank Professor Rutherford for the kind interest he has taken during the progress of this research.

Physical Laboratory, University of Manchester.

Note added March 12, 1908.—Since the above was communicated a paper has been published by E. Meyer and E. Regener in the Verhandlungen der deutschen physikalischen Gesellschaft, No. 1, 1908. The authors also find, using a different method to the writer, that the error increases with the square root of the intensity of the radiation. Further, they state that by measuring the error  $\epsilon$  and the saturation current i the charge of an ion may be determined. But the calculation involves the number of ions produced by an  $\alpha$  particle, and this number was determined by Rutherford under the assumption that the charge of an  $\alpha$  particle is identical with the charge of an ion. This, however, is still an unsettled question.

I may add here that the number of  $\alpha$  particles emitted per sec. from a given substance can be determined directly by simply measuring the error  $\epsilon$  and the saturation current i. For the error  $\epsilon$  in E.S.U. is given by

$$\epsilon = \pm Ne \sqrt{Z}$$

where N is the number of ions produced by one  $\alpha$  particle, e the charge of an ion, and Z the number of particles emitted per sec., while the saturation current is given in E.S.U. by

$$i = NeZ$$
.

By division we get Z as function of  $\epsilon$  and i only. The agreement between the errors determined by theory and by experiment indicates that the calculated number of  $\alpha$  particles emitted per sec. from a radioactive body of known activity is of the right order of magnitude.

LI. Further Measurements of Wave-lengths, and Miscellaneous Notes on Fabry and Perot's Apparatus. By Lord Rayleigh, O.M., P.R.S.\*

IN a former paper † I described a modified form of apparatus and gave the results of some measurements of wavelengths, partly in confirmation of numbers already put forward by Fabry and Perot and partly novel, relating to helium. I propose now to record briefly some further measures by the same method, together with certain observations and calculations relating thereto of general optical interest.

The apparatus was arranged as before, the only change being in the interference-gauge itself. The distance-pieces, by which the glasses are kept apart, were now of *invar*, with the object of diminishing the dependence upon temperature. The use of invar for this purpose was suggested by Fabry and Perot, but I do not know whether it has actually been employed before. The alloy was in the form of nearly spherical balls, 5 mm. in diameter, provided with projecting tongues by which they were firmly fitted to the iron frame. The springs, holding the glasses up to the distance-pieces, were of the usual pattern. The whole mounting was constructed by Mr. Enock, and it answered its purpose satisfactorily. There is no doubt, I think, as to the advantage accruing from the use of invar.

The measurements were conducted as explained in the earlier paper. The first set related to zinc which was compared with cadmium. Both metals were used in vacuum-tubes, of the pattern already described, with electrodes merely cemented in. It was rather to my surprise that I found ordinary soft glass available in the case of zinc, but no difficulty was experienced. The former observations with the "trembler" suggested a wave-length for zinc red about one-millionth part greater than that (6362·345) given by Fabry and Perot. This correction has been confirmed, and I would propose 6362·350, as referred to Michelson's value of the cadmium red, viz. 6438·4722. No difficulty was experienced in identifying the order of the rings by the method formerly described and dependent upon observations with the gauge alone.

The results of the measurements upon helium were not in

<sup>\*</sup> Communicated by the Author.

<sup>†</sup> Phil. Mag. [6] vol. xi. p. 685 (May 1906).

quite such close accord with the earlier ones as had been expected. Both sets are given below for comparison.

Wave-lengths of Helium.

III.
7065.200
6678.150
5875.625
5015.680
4921.930
4713.144
4471.482

The two last entries under II., enclosed in parentheses, were obtained with the 1 mm. apparatus, and could not be expected to be very accurate. Preference may be given to III. throughout.

These measurements of wave-lengths were not further pursued, partly because it was understood that other observers were in the field and partly because my own vision, though not bad, is less good than it was. In particular at the blue end of the spectrum I found difficulty. It is evident that work of this sort should be undertaken only under the best conditions.

One of the less agreeable features of the method is the complication which arises from the optical distance between the surfaces being slightly variable with the colour. In the earlier observations with a 5 mm, apparatus I was surprised to find the change amounting to  $2\frac{1}{2}$  parts per million between cadmium red and cadmium green. In the light of subsequent experience I am disposed to think that the silver surfaces must have been slightly tarnished. At any rate in the later measurements I found the difference much less, indeed scarcely measurable. It will be understood that no final uncertainty in the ratio of wave-lengths arises from this cause. Whatever the change may prove to be, it can be allowed for.

#### Thirty Millimetre Apparatus.

In this instrument the object was to construct a gauge with a much greater distance than usual between the plates, but otherwise on the same general plan as that of Fabry and Perot. The distance-piece A A, fig. 1, consisted of a 30 millimetre length of glass tubing, each end being provided with three protuberances, equally spaced round the circumference,

at which the actual contacts took place. The removal of the intervening material and the shaping of the protuberances

were effected with a file moistened with turpentine.

Against this distance-piece the glass plates BB are held by the arrangement shown in fig. 1. The lower plate B rests upon a brass ring C to which the brass castings D are rigidly attached. The upper ring E is connected with the castings only through the steel springs F. Both rings are provided with protuberances in line with those on the glass cylinder, and the pressure is regulated by the screws G. The whole was constructed by Mr. Enock. Some little care is required in putting the parts together to avoid scratching the half-silvered faces; but when once the apparatus is set up its manipulation is as easy as that of the ordinary type.

In all interference-gauges it is desirable that the distancepieces be adjusted as accurately as possible. For although a considerable deficiency in this respect may be compensated by regulating the pressures (see below), the adjustment thus arrived at is less durable, at least in my experience. Even when the distance-pieces are themselves well adjusted, it is

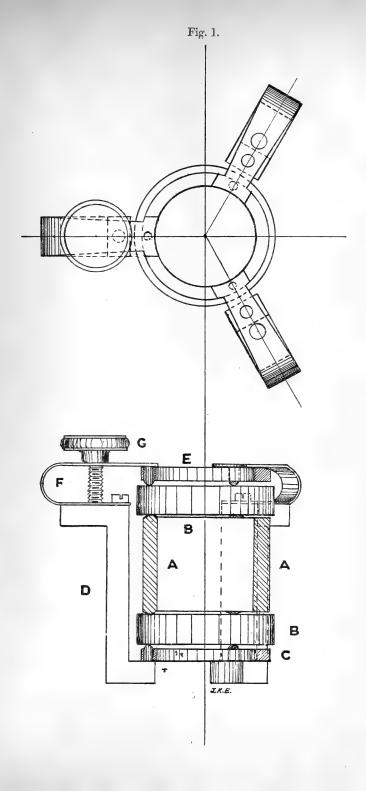
advisable to employ only moderate pressures.

Observations with the 30 mm. gauge have been made upon helium, thallium, cadmium, and mercury. In the first case the (yellow) rings are faint, the retardation being not far from the limit. Indeed when at first it was attempted to adjust the plates with helium, the rings could not be found. With thallium also the rings were rather faint, but with mercury and cadmium there was no difficulty.

## Magnifying Power.

At a distance of 30 mm. the rings are rather small, and one is tempted to increase the magnifying power of the observing telescope. As to this there should be no difficulty if the aperture could be correspondingly increased. But although the plates themselves may be large enough, an excessive strain may thus be thrown upon the accuracy of the figuring and upon the adjustment to parallelism. If, on the other hand, the aperture be not increased, the illumination of the image falls and the extra magnifying may do more harm than good.

A means of escape from this dilemma is to effect the additional magnification in one direction only, which in the present case answers all purposes. When straight interference-bands, or spectrum lines, are under observation, there is no objection to astigmatism, and we may merely



replace the ordinary eyepiece of the telescope by a cylindrical lens or by a combination of spherical and cylindrical lenses. This arrangement can be employed in the present instance, but the result is not satisfactory. A complete focusing, leading to a point-to-point correspondence between image and object, may however be attained by suitably sloping the object-lens of the telescope. In this way excellent observations upon interference-rings are possible under a magnifying power which otherwise would be inadmissible, as entailing too great a loss of light. The subject will be more fully treated in a special paper.

## Adjustment for Parallelism.

If the surfaces are flat, and well-adjusted, Haidinger's rings depend entirely upon obliquity. A slight departure from parallelism shows itself by an expansion or contraction of the rings as the eye is moved about so as to bring different parts of the surfaces into play. In making this observation the eye must be adjusted to infinity, if necessary with the aid of spectacle-glasses, and it may be held close to the plates; but a telescope is not needed or even desirable. If the departure from parallelism be considerable, no rings at all are visible; but there is an intermediate state of things where circular arcs may be seen by an eye drawn back somewhat and focussed upon the plates.

The character of these bands is intermediate between those of Newton's and Haidinger's rings, the retardation depending both upon the varying direction in which the light passes the plates and reaches the eye and also upon the varying local thickness. If we take as origin of rectangular coordinates in the plane of the plates, the place corresponding to normal passage of the light, the retardation due to obliquity is as  $-(x^2+y^2)$ . The retardation due to local thickness is represented by a linear function of x and y, so that the variable part of it may be considered to be proportional to x. Hence the equation of the bands is

$$\alpha x - x^2 - y^2 = \text{constant},$$

 $\alpha$  being positive if x is considered positive in the direction of increasing thickness. Accordingly the bands are in the form of concentric circles and the coordinates of the centre are

$$x = \frac{1}{2}\alpha, \qquad y = 0.$$

When curved arcs are seen by an eye looking at the plates perpendicularly, the greatest thickness lies upon the concave

side of the arcs. The perpendicular direction of vision may be tested by observing the reflexion of the eye itself in the silvered surface.

#### Behaviour of Vacuum-Tubes.

The form of vacuum-tube described in the first paper, and depending on sealing-wax for air-tightness, continues to give satisfaction. As already mentioned, though made of soft glass, they are available for zinc, and the cadmium tubes have lasted well with occasional re-exhaustion. It is advisable to submit them to this operation when the red light begins to fall off. After one or two re-exhaustions the condition seems to be more durable.

With thallium my experience has been rather remarkable. The green light is very brilliant and offers a further advantage as being comparatively free from admixture with other colours\*. But Fabry and Perot found thallium tubes to be very short-lived, sometimes lasting only a few minutes. I have used but one thallium tube, of the same construction as the others, and charged with a little thallium chloride. This tube has been used without special care on many occasions—I cannot say how many, but probably seven or eight times,—and it does not appear to have deteriorated at all. It looks as though the chloride had decomposed and metal had deposited upon the aluminium electrodes. But what the circumstances can be that render my experience so much more favourable I am at a loss to conjecture.

The same form of tube answers well for mercury, but with this metal there is usually no difficulty.

#### Control of the figure of the glasses by bending.

Very good plates can now be procured from the best makers, but on careful testing they usually show some deficiency, mostly of the nature of a slight general curvature. Thus when in Fabry and Perot's apparatus the adjustment for parallelism is made as perfect as possible, the rings may be observed to dilate a little as the eye moves outwards in any direction from the centre towards the circumference of the plates. This indicates a general convexity.

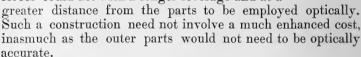
It occurred to me that an error of this kind might be approximately corrected by the application of bending forces to one of the plates—it does not matter which. The easiest way to carry out the idea is to modify the apparatus in such a way that the points of application of external pressure are

<sup>\*</sup> The green line is known to be itself double.

not exactly opposite the contacts with the distance-pieces, but are displaced somewhat inwards or outwards in the radial direction (fig. 2). If the plates are too convex, the

Fig. 2.

points of pressure must be displaced outwards. In this form I have tried the experiment with a certain degree of success, but the displacements that I could command (1 mm. only) were too small in relation to the thickness of the plate. If it were intended to give this plan a proper trial, which I think it would be worth in order to render a larger aperture than usual available, the plates, or at least one of them, should be prepared of extra diameter, so that the bending forces could act with a longer leverage and at a



It may be worth while to consider the question here raised more generally. The problem is so to deform one surface, by forces and couples applied at the boundary, as to compensate the joint errors of the two surfaces and render the distance between them constant. If we take rectangular coordinates x, y in the plane of the surface with origin at the centre, the deformation obtainable in this way is expressed by terms in the value of  $\xi$  (the other coordinate of points on the surface) proportional to  $x, y, x^2, xy, y^2, x^3, x^2y, xy^2, y^3$ . For such terms are arbitrary in the solution of the general equation of equilibrium of a plate, viz.

$$\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2}\right)^2 \zeta = 0.$$

Of these terms those in x and y correspond of course merely to the adjustment for parallelism, and those of the second degree to curvature at the centre. The conclusion is that we may always, by suitable forces applied to the edge, render the distance between the plates constant, so far as terms of third order inclusive.

Another inference from the same argument is that, in any optical apparatus, approximately plane waves of light may be freed from curvature and from unsymmetrical aberration (expressed by terms of the third order) by means of reflexion at a plate to the boundary of which suitable forces are applied. And the surface of the plate need not itself be more than approximately flat.

### Figuring by Hydrofluoric Acid.

It would be poor economy to employ any but the best surfaces in measuring work needing high accuracy; but there are occasions when all that is needed can be attained by more ordinary means. Common plate-glass is rarely good enough\*; but I have found that it can be re-figured with hydrofluoric acid so as to serve fairly well, and the process is one of some interest. From what has been said already it will be understood that it is not necessary to make both surfaces plane, but merely to fit them together, which can be effected by operations conducted upon one only.

Pieces of selected plate-glass, about \(\frac{1}{4}\) inch thick and of a size suited to the interference-gauges, were roughly shaped by chipping. The best surfaces were superposed and the character of the \(\frac{fit}{it}\) examined by soda-light. One glass being rotated upon the other, the most favourable relative azimuth was chosen; and by means of suitable marks upon the edges the plates were always brought back to the chosen

position.

The principles upon which the testing is conducted have been fully explained in a former paper. In the present case the surfaces are so close to one another that no special precautions are required. With a little management the contact is so arranged that a moderate number of bands are visible. If the fit were perfect, or rather if the surfaces were capable of being brought into contact throughout, these bands would be straight, parallel and equi-distant. departure from this condition is an error which it is proposed to correct. The sign of the error can be determined without moving the glasses by observing the effect of diminishing the obliquity of reflexion, which increases the retardation. Thus if a band is curved, and the change in question causes the band to move with convexity forwards. it is a sign that material needs to be removed from the parts of the glass occupied by the ends of the band. Such an operation will tend to straighten the band. If, however, the movement take place with concavity forward, then material needs to be removed from the middle parts. In every case the rule is that by removal of glass the bands, or any parts of them, can be caused to move in the same

cially if the magnification used is in one direction only.

† "Interference Bands and their Applications," 'Nature,' xlviii.

p. 212 (1893); Scientific Papers, iv. p. 54.

<sup>\*</sup> If the surfaces are so shaped that the interference-bands presented on superposition are hyperbolic, much may be gained by limiting the aperture to a narrow slit corresponding to one of the asymptotes, especially if the magnification used is in one direction only.

direction as that in which they move when the obliquity of reflexion is diminished.

In carrying out the correction, the plate on which it is intended to operate is placed below, and it is convenient if it be held in some form of steady mounting so that the upper plate can be removed and replaced in the required position without trouble. The acid, two or three times diluted, is applied with a camel's hair brush and after being worked about for a few seconds is removed suddenly with a soft cloth. Endeavour should be made to keep the margin of the wetted region moving in order to obviate the formation of hard lines. Success depends of course upon judgement and practice, and the only general advice that can be given is to make a great many bites at the cherry, and to keep a record of what is done each time by marking suitably on one of a system of circles drawn upon paper and representing the surface operated on. After each application of acid the plates are re-examined by soda-light and the effect estimated. The difficulty is that in most cases the bands are not reproduced in the same form. In one presentation the error may reveal itself as a curvature of the bands and in another as an inequality in the spacing of bands fairly Often by a little humouring the original form may be approximately recovered, and in any case the general rule indicates what needs to be done.

By this method I have prepared two pairs of plates which perform very fairly well, but of course only when placed in the proper relative position. The operations, though prolonged, are not tedious, and I doubt not that with perseverance better results than mine might be achieved. The surface of the glass under treatment suffers a little from the development of previously invisible scratches in the manner formerly explained, but the defect hardly shows itself in actual use. I have not ventured to apply the method to surfaces already very good such as those supplied by the best makers for use in Fabry and Perot's apparatus; but I should be tempted to do so if I came across a pair suffering from slight general concavity. The application of acid would then be at the outer parts. In the best glasses that I possess the error is one of convexity.

# Effect of Pressure in Fabry and Perot's Apparatus.

The observation that the rings were more sensitive than had been expected to the pressure by which the plates are kept up to the distance-pieces, led to a calculation on Hertz's theory of the relation between the change of interval and the pressure. If two spheres of radii  $r_1$  and  $r_2$  and of material for which the elastic constants in Lamé's notation are  $\lambda_1$ ,  $\mu_1$ ,  $\lambda_2$ ,  $\mu_2$ , are pressed together with a force P, the relation between P and the distance ( $\alpha$ ) through which the centres approach one another, as the result of the deformation in the neighbourhood of the contact, is

$$P = \frac{4}{3\pi} \left( \frac{r_1 r_2}{r_1 + r_2} \right)^{\frac{1}{2}} \frac{\alpha^{\frac{3}{2}}}{\theta_1 + \theta_2}^*,$$

where

$$\theta_1 = \frac{\lambda_1 + 2\mu_1}{4\pi\mu_1(\lambda_1 + \mu_1)}, \quad \theta_2 = \frac{\lambda_2 + 2\mu_2}{4\pi\mu_2(\lambda_2 + \mu_2)}.$$

In the case of materials which satisfy Poisson's condition,  $\lambda = \mu$ , and we may take as sufficiently approximate

$$\theta_1 = \frac{3}{8\pi\mu_1}, \quad \theta_2 = \frac{3}{8\pi\mu_2};$$

so that

$$\mathbf{P} = \frac{32}{9} \left( \frac{r_1 r_2}{r_1 + r_2} \right)^{\frac{1}{2}} \frac{\mu_1 \mu_2 \alpha_2^{\frac{3}{2}}}{\mu_1 + \mu_2}.$$

In the application that we have to make, one of the spheres is of steel (invar) and of radius  $r_1 = .25$  cm., while the other is of glass and of radius  $r_2 = \infty$ . Further, for the steel we may take  $\mu_1 = 8.2 \times 10^{11}$ , and for glass  $\mu_2 = 2.4 \times 10^{11}$ , and thus

$$P = 3.30 \times 10^{11}$$
,  $\alpha^{\frac{3}{2}}$ ,

 $\alpha$  being in cm. and P in dynes. It will be convenient for our purpose to reckon  $\alpha$  in wave-lengths (equal say to  $6 \times 10^{-5}$  cm.) and P in kilograms, taking the dyne as equal to a milligram weight. On this understanding

$$P = 15 \alpha^{\frac{3}{2}},$$

signifying that to cause an approach of one wave-length the force required is 15 kilogram. If P and α undergo small

\* See Love's Math. Theory of Elasticity, § 139.

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variations,

$$dP = \frac{3}{2} (.15) \alpha^{\frac{1}{2}} d\alpha = \frac{3}{2} (.15)^{\frac{2}{3}} P^{\frac{1}{3}} d\alpha,$$

 $dP/d\alpha$  being somewhat dependent upon the total pressure P. For the purposes of experiment a spring-balance was mounted upon the frame of the apparatus (carrying the distance-pieces) so as to diminish the pressure exerted over one of the distance-pieces, that is to diminish the pressure by which one of the plates was held up to one of the distancepieces. Starting from perfect parallelism of the plates and keeping the eye carefully fixed so as to receive the light from the centre of the plates, it was observed that to cause a shift of one band (helium vellow) the spring-balance needed to exert a pull of '78 kilo. At this stage the plates were of course no longer parallel and a moderate shift of the eve would cause a displacement independently of any change in the spring-balance. At the same time the rings lost their sharpness. On this account it is hardly practicable to use a shift of more than one band, and indeed a smaller shift of half a band was usually preferred. The total force required to compensate the spring of the apparatus, and so to relieve the compression of the distance-piece on this side, was 2.4 kilos. This is what is represented by P in the above formula, while dP = -.78.

In order now to compare theory and observation we must remember that the one band (corresponding to half a wavelength) observed at the centre implies three times as great a shift at the particular distance-piece where alone the force was varied. Thus the observed dP corresponds to  $d\alpha = -\frac{3}{2}$ . For this  $d\alpha$ , the calculated dP is

$$dP = -\frac{9}{4} (.15)^{\frac{2}{3}} (2.4)^{\frac{1}{3}} = -.85 \text{ kilo.}$$

The agreement with the observed -78 is certainly as good

as could have been expected.

In considering what differences of distance are to be expected when the plates are adjusted to parallelism under different pressures, we must remember that the above calculation and observation relates to the compression which may occur at the contact of a single distance-piece with a single plate. There are in all six contacts of this kind, and we may conclude that when no special pains are taken to regulate the absolute pressures employed, a shift of 6 bands or more on remounting need not cause surprise.

LII. The Positive Column in Oxygen.

By the Rev. P. J. Kirkby, Fellow of New College, Oxford\*.

SOME researches in which I have recently been engaged led me to investigate the electric force in the "positive column" when a steady electric discharge passes through oxygen at low pressures between two plane parallel electrodes

placed in a straight glass tube.

The "positive column" in such a cylindrical discharge may, in view of common experience, be defined as a region of the discharge terminating at or close to the anode or positive electrode where the electric force—i. e. the potential difference per centimetre—is constant or nearly constant. Close to the cathode there is an abrupt fall of potential called the "cathode fall." Here there is a bright glow lining the cathode which is unmistakable. Between this glow and the positive column there is nothing to catch the eye at pressures of a few millimetres of mercury. The positive column is easily recognized as a long faintly luminous column of a colour which varies with the gas through which the discharge passes, being in oxygen either pale violet or a curious green.

At pressures of the order 1 mm, it begins at a distance of about 6 cms, from the cathode and extends right up to the anode. The nearest point of the positive column to the cathode may be called the *foot* of the positive column. The electric force is remarkably constant throughout this region: it depends chiefly on the pressure, but is said to vary † to some extent with the diameter of the discharge-tube.

The results of my experiments show that in oxygen the variation of the electric force in the positive column with the pressure presents exceptional features which do not appear to have been noticed. In the first place, the force is very much smaller than in the other common gases; secondly, instead of diminishing continually with the pressure it reaches a minimum at about 2.0 mms. pressure; and thirdly, there is a sharp discontinuity in its value at a pressure of .8 mm. as measured by the McLeod gauge.

The methods hitherto employed to investigate the electric force in the positive column have generally involved the use of exploring wires fused into the sides of the tubes: their difference of potential during a discharge divided by their distance apart was assumed to give the electric force in the undisturbed gas. This method is open to the criticism that

<sup>\*</sup> Communicated by the Author.

<sup>†</sup> J. J. Thomson, 'Conduction of Electricity through Gases,' ch. xv.

the introduction of the wires in the sides must disturb the uniformity of the surface of the discharge-tube, and pre-

sumably affect the discharge itself.

The method which I employed did not involve the use of an exploring wire. It is the same which I used to determine the force in the positive column in a discharge through

electrolytic gas \*.

It depends on the assumption, suggested by experience and, I believe, fully justified by these experiments, that the positive column can be lengthened without making any other sensible change in the steady discharge. Throughout this paper;

D represents the distance in cms. between the electrodes, always exceeding the distance between the foot of the positive column and the cathode;

C the steady current passing through the gas and always

·0025 ampere;

X the voltage-difference of the electrodes during the discharge;

Y the electric force in volts per cm. in the positive column; and

p the pressure in mms. of mercury.

Then if D is increased by d, the potential-difference of the electrodes required to maintain the same current C as before under the same conditions will be simply X + Yd.

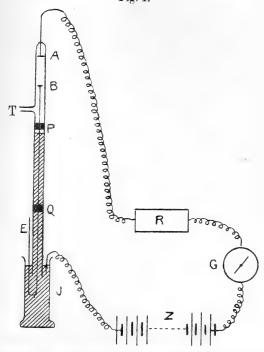
In fact if everything is kept constant in the discharge but X and D, X will obviously be a continuous function of D whatever D's value. If D is taken as abscissa and X as ordinate a curve can be plotted, and it is easy to verify under favourable conditions that when D exceeds a certain value the curve becomes straight within the limits of experimental error, and that the value in question is about the distance of the foot of the positive column from the cathode. The slope of this straight part of the D-X curve is obviously the electric force Y in the positive column. The advantage of this method is first that the exploring wire is dispensed with, and secondly that the electric force can be determined and verified by several observations with different values The disadvantage is that the observations are not simultaneous, so that if a small change occurs in the region of the discharge near the cathode, where the electric force is very great, relatively large errors may occur in the observa-This difficulty should only be felt when Y is small; but in oxygen Y is remarkably small, ranging for pressures

<sup>\*</sup> Phil. Mag. March 1907.

less than 5 mm. between 4.5 and 20 volts per cm. in these experiments. Now the cathode fall is about 400 volts, so that if a small change of a few per cent. in the field near the cathode occurs between two observations, it can easily introduce an error of 1 cm. in D. Moreover, it is necessary to keep the current accurately the same, since a very small error in reading it corresponds to a much larger one in D.

The electrical arrangement is represented diagrammatically in fig. 1. ABPQ represents the discharge-tube, supported in such a position that its base dipped under the mercury filling a large jar J. The side tube T connected the discharge-tube through a drying-tube to a mercury pump, and to an electrolysis apparatus where oxygen was generated and dried. It may be stated here that the oxygen was prepared by the electrolysis of pure barium hydrate, which insures its purity\*.

Fig. 1.



The figure represents the tube partly filled by the mercury—the shaded part—when the oxygen was reduced to a low pressure. A is the fixed cathode connected to a platinum

<sup>\*</sup> H. B. Baker, Trans. Chem. Soc. 1902, vol. lxxxi.

wire fused into the top of the tube. The anode B is attached to an iron rod, which, sliding in the fixed steel guides P, Q, and bent round the bottom, terminates at E. Thus by raising or lowering E, the movable anode could be adjusted to any distance up to about 30 cms. The positive end of the battery Z was in metallic connexion with the mercury, and so with the anode; and the negative end was connected through a galvanometer G and the variable resistance R to the cathode A. Z was usually of about 1500 volts, G was a high resistance and dead-beat voltmeter, and R several 100,000 ohms.

With such an apparatus R could be varied and D determined by adjusting the anode till the galvanometer recorded C. And then we may, as stated above, regard X as a linear

function of D, C and p being constant.

Now X and R are connected by the ohmic equation

$$X = Z - C(R + G),$$

if Z denotes the E.M.F. of the battery and G the resistance of the galvanometer, together with any other invariable resistance in the circuit including that of the battery. Therefore R is a linear function of D, and the points whose coordinates are D, R will determine a straight line, the slope of which multiplied by C is the electric force in the positive column, since

$$Y = \frac{dX}{dD} = -C\frac{dR}{dD}$$
.

The slope of the D-R line was determined throughout the earlier experiments by finding the values of D corresponding to several different values of R. Thus a number of points were plotted, which, if the discharge had been steady, lay upon or close to a straight line. If they did not, I often found that some lay very near one line and others fell close to a line parallel and close to the former. showed in rather an interesting way that the discharge had shifted from one to the other of two slightly different states or positions without, however, affecting the magnitude of the force in the positive column. Sometimes three such parallel lines could be recognized, but of course, if there were more than two such shifts, the corresponding parallel lines cannot easily be detected, and the force Y can only be estimated, and with considerable error, by drawing the mean locus of the points. Owing to this experience and in order to obviate such shifts, I ultimately determined Y, when possible, in a single discharge by diminishing R twice by the same amount r-i.e. by 2r altogether—and determining the corresponding increases  $d_1$ ,  $d_1+d_2$  to D. If  $d_1$  was nearly equal to  $d_2$ , it was assumed that no alteration had occurred in the discharge outside the positive column to invalidate the experiment; the force Y was taken to be the mean of  $\frac{Cr}{d_1}$  and  $\frac{Cr}{d_2}$ , and

the difference between  $d_1$  and  $d_2$  compared with either as an index of the experimental error. This method is useful when

the discharge is unsteady.

When the pressure is less than its value at which Y is discontinuous,  $d_1$  is always nearly equal to  $d_2$ , for the points whose coordinates are D, R fall accurately upon a straight line. But for pressures above '8 mm, it is seldom that the discharge remains constant enough to permit the determination of Y with the same precision. The chief cause of variation is the flickering of the discharge which at the higher pressures does not cover the whole of the cathode nor remain on the same part of it. And if the electrodes become oxidized the trouble increases.

After making experiments with zinc and nearly pure silver electrodes and being much inconvenienced by their oxidation, I tried silver-gilt electrodes. These were much the most satisfactory, and as long as the gold lasted no sign of discolouration appeared on the cathode or discharge-tube. The anode deepened in colour, but only tarnished where the gold was obviously thinnest. The cathode closely fitted the discharge-tube whose diameter was nearly 2.4 cms. The diameter of the anode was 2 cms., so that it could move up and down the tube without touching it.

Table I.

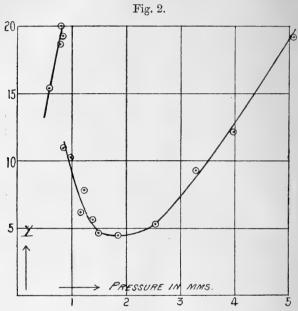
p.	Y.	p.	Y.	p.	Y.
2.52	5.3	5 06	19.2	3.94	12.1
1.85	4.5	3.28	9.3	.96	10.2
1.48	4.6	1.38	5.7	.802	20.0
.804	110	1.16	6.25		
.802	19.2	.56	15.4	1.21	7.8
.79	18.7				

The results of experiments with these electrodes are given in Table I., each compartment of which applies to a fresh quantity of oxygen. The errors in the determination of Y

during a given discharge are estimated to be 4 or 5 per cent. except for pressures below 8 mm., when the results are much more accurate. The pressures were all measured upon a McLeod gauge.

Table I. is illustrated by the curve in fig. 2, in which all the points lie satisfactorily near the curve except two, the determinations of which were more uncertain than that of

the others.



The curve is entirely different from corresponding curves of the other common gases. When p is greater than 1.5 mm. the values of Y are only between one-tenth and one-fifth of the electric force in a similar positive column in the similarly dense gases nitrogen or carbon monoxide. Again, at the pressure 1.75 mm., Y reaches a minimum with the curiously small value 4.5 volts per cm.

The third peculiar and most interesting feature of the curve is the violent discontinuity which Y undergoes at the pressure '8 mm. That the discontinuity is real and not apparent is shown by the fact that Y then passes suddenly from about 11 to 20 without seeming to assume any intermediate value, and even more by the fact that a complete change seems to come over the discharge, which now settles down into the greatest steadiness. Thus the curve is broken and not merely very steep. The change occurs during a

discharge, if the pressure of discontinuity is approached very gradually. I have twice noticed immediately after the sudden rise in Y the appearance of peculiar striæ so close together that there were 10 within 1.8 cm. That was with the zinc electrodes. It is very seldom indeed that they appear with

oxygen.

To investigate the discontinuity in Y more thoroughly, I connected to the apparatus a large glass tube which could be filled partly or wholly with mercury like the barrel of a mercury pump. With this arrangement the pressure could be varied, and, without introducing new oxygen, could be made to pass backwards and forwards across the point of discontinuity. It was then observed that Y passed from its low value to its high and back again from high to low, keeping pace with the pressure. This is illustrated by the following simultaneous values of p and Y, which represent a series of experiments upon the same mass of oxygen:—

·95 mm., 10; ·84, 11·4; ·765, 19·2; ·802, 20·0; ·88, 11·6; ·81, 20.

It is evident, therefore, that the discontinuity is not brought about because the gas has been vitiated by the discharge. It must be due to some inherent instability in the oxygen when

the pressure is slightly greater than '8 mm.

But when a quantity of oxygen had been subjected to a long series of discharges, the pressure can be raised considerably beyond '8 mm. where the discontinuity first occurred. Thus on one occasion, after the pressure was reduced below the discontinuity point, it was gradually raised from '79 mm. to 1.07 without Y's abruptly changing, and Y reached the abnormally high value 23. The same phenomenon was observed with the silver electrodes.

The electric discharge therefore *tends* to prevent the oxygen from recovering the condition roughly defined by p=8, Y=11. It is natural to attribute this tendency to ozone; especially since the fall of pressure during each of these two series of observations showed the conversion of a considerable amount—probably more than 15 per cent.—of

oxygen into ozone.

We may therefore conclude that the presence of ozone checks the repassage of the oxygen through the discontinuity.

When the pressure falls below '8, the slope of the curve p-Y is very steep; but there is no discontinuity whatever here. On the contrary, Y is nowhere determined so easily as when p lies between '5 and '8 mm. The discharges for this range of pressures are very steady: the readings of D

are repeated with little error, and the decrease in R, and therefore the increase in X, is strictly proportional to the increase in D—facts which prove that very little change occurs in the region of high force near the cathode during a series of discharges with the same current. This steadiness is shown by Table II., which gives the results of a series of experiments with gradually diminishing pressure upon freshly introduced oxygen during my earlier experiments with zinc electrodes (diameter 2·1 cms.). The total duration of the discharges used for these observations was about

TABLE II.

$p_{\cdot}$	Y.	25·6 p+·9.	
.804	21.4	21.5	
·75	19.8	20.1	
·72	19.2	19:3	
.69	18.35	18.5	
.66	17.85	17.7	
•643	17.25	17:35	
617	16.8	16.7	
·58	15.8	15.7	
•534	14.42	14.55	

3 minutes; and it may be taken that ultimately 10 per cent. of the gas was ozone. The numbers show an extremely accurate agreement, and prove that the curve is very straight to the left of the discontinuity; for every value of Y but one differs from 25.6 p + 9 by less than 1 per cent.

Table II. exhibits great consistency in the observations, which were made rapidly, and all but the first and last with two observations only. In fact it is experiments like these, made with a steady discharge, that establish the validity of the method and prove that the positive column can be lengthened without otherwise sensibly affecting the discharge. We can also infer from the table that the presence of a good deal of ozone does not greatly modify the force Y when p is less than '8.

Table III. contains the results of experiments, other than those in Table II., made with the zinc electrodes. The percentage errors in the values of Y, most of which were determined by several observations, is not more than 4 and in

most cases less than 2 or 3. Each compartment of Table III. applies to experiments upon the same specimen of oxygen.

TABLE III.

p.	Y.	p.	Y.	p.	Y.
1.02	7.5	6.26	15	1.02	7.5
•495	13.1	4.2	6.6	. 79	20.4
		3.2	5.25		
2.02	4.6	2.42	4.04	.785	20.4
				.73	19.2
4.0	8.2	2.9	5.9	.7	17.6
2.36	4.4	.686	17.8		
1.49	6.15	•49	12.5	·88	11.7

The numbers in Table III. are with two exceptions sufficiently concordant, although the oxygen had in many cases been subjected to much discharge. They determine a curve which is nearly identical with that of fig. 2 for pressures below 2 mms., but falls much below it when p exceeds 2 mms. Thus, when p exceeds 4, Y is less than two-thirds of its corresponding value in fig. 2. This large difference cannot be attributed to the small difference in the discharge-tubes; especially since the latter difference should make—if we can be guided by the behaviour of nitrogen \*—the values of Y in Table III. greater than those in Table I.

Hence the conclusion is forced that the divergence is due to the use of different electrodes. This conclusion is confirmed by my experiments with silver electrodes, which gave a general agreement with the foregoing results for pressures less than 2.5 mms., and at first gave the usual pressure of discontinuity. But partly perhaps owing to the cathode's not fitting the tube, and chiefly, I believe, to the oxidation of the electrodes, these experiments left few numbers to rely on or worth recording. It may be remarked, however, that when the electrodes became badly attacked, the pressure of discontinuity was thrown back to the point 62 mms., and the values of Y on both sides of it were then reduced to 8 and 18.

<sup>\*</sup> Herz found that the electric force in nitrogen was 99.7 and 89.3 for tubes 10 and 20 mms. in diameter respectively.—J. J. Thomson, l. c. ch. xv.

The observation of the discontinuity in Y at the pressure '8 mm. immediately recalled the discontinuity of pv observed by C. Bohr \* in oxygen at the pressure '7 mm., the history of which is very interesting. Bohr's observations were confirmed by Baly and Ramsay †; but in 1901 Lord Rayleigh ‡ was unable to detect any signs of such an effect with his extremely accurate manometer, and, at a loss to account for the difference between Bohr's experience and his own, could "only suppose that it must be connected somehow with the quality of the gas complicated perhaps by interaction with the glass or the mercury."

Now, according to Bohr, Boyle's law must be replaced, in the case of oxygen, for temperatures between 11 and 14, by

and by  $(p+\cdot 109)v = k$  when p is greater than '7 mm.,  $(p+\cdot 07)v = k$  when p is less than '7 mm.

All the pressures given above were measured on a McLeod gauge: and the temperature of the laboratory ranged from 10° to 15°. Hence, if Bohr's results apply to them, they must be diminished by 109 when p is greater than 7 mm., and by 07 when p is less than 7 mm. Moreover, the pressure 7 would be given by the McLeod gauge either as 809 or 77. Thus the pressure of Bohr's discontinuity agrees in the closest way with the pressure at which Y is discontinuous. Nevertheless, in view of Lord Rayleigh's conclusions, I have not ventured to make any corrections to the estimated values of my pressures.

The observed discontinuity in Y points to a molecularly unstable condition reached by oxygen at the pressure in question, such that under the discharge the gas—or possibly only that part of it which is the seat of the discharge—passes from one to the other of two states of molecular equilibrium. In this connexion the suggestion of Sutherland § in explanation of Bohr's and Sir W. Crookes's anomalies is interesting, that oxygen tends spontaneously to pass into ozone at about '7 mm. pressure. This view receives some support from the conclusion above that the presence of ozone checks the return of the oxygen to the state defined by smaller values of Y. I have twice observed at the point of Y's discontinuity curious falls of pressure which would be well explained by Bohr's results, and cannot but conclude that his

<sup>\*</sup> Wied. Ann. vol. xxvii. pp. 459-479 (1886).

<sup>†</sup> Phil. Mag. vol. xxxviii. p. 301 (1894). ‡ Phil. Trans. 1901, p. 205.

<sup>§</sup> Phil. Mag. vol. xliii. 1897, p. 201.

discontinuity and the discontinuity in Y are intimately connected. Is it not a possible explanation of Lord Rayleigh's and Prof. Bohr's different experiences, that the carefully dried tubes of the latter may have developed a high state of electrification by the motion of the mercury, and that thus the gas became subject to electrical disturbances sufficient to effect the transition from one molecular state to the other?

These experiments were made in the laboratory of Prof. J. S. Townsend, Wykeham Professor of Physics, Oxford.

### LIII. Notices respecting New Books.

Condensation of Vapor as induced by Nuclei and Ions. By CARL BARUS, Hazard Professor of Physics, Brown University. Washington: Published by the Carnegie Institution. 1907. Pp. ix+164.

In this monograph the author, whose work on nuclei is well known, describes a number of investigations carried out with his fog-chamber apparatus. The apparatus having been sufficiently improved, it was used for various experiments, including the growth of persistent nuclei, the production of water nuclei by evaporation, the results obtained when X-rays are allowed to strike the fog-chamber from different distances, the effect due to radium, &c. Other problems dealt with in the book are the distribution of colloidal nuclei and of ions in media other than airwater, the simultaneous variation of the nucleation and the ionization of the atmosphere of Providence, and the variations of the colloidal nucleation of dust-free air in course of time.

Fourier's Series and Integrals. By H. S. Carslaw. Macmillan and Co. London and New York. 1906.

The complete title is "Introduction to the Theory of Fourier's Series and Integrals and the Mathematical Theory of the Conduction of Heat." The book naturally falls into two parts, Part I. being concerned with the purely mathematical developments, and Part II. with the applications to the various practical and ideal problems of heat conduction. Basing on the modern theory of rational and irrational numbers, Professor Carslaw leads up through a logical discussion of the convergence of infinite series to the important forms associated with the name of Fourier, finishing in Chapter VIII. with the Integrals. This part occupies 187 pages in a book of 430 pages. The remainder is devoted to the problems of thermal conduction. Professor Carslaw is to be congratulated on supplying a book which cannot fail to be of great service to several classes of readers. The student of pure mathematics will find his mind directed along the best modern lines of investigation of

an important set of functions; and he will find opportunity of testing his powers by consideration of the examples which are appended to most of the Chapters in Part I. The physicist, again, who is face to face with a practical problem will find, if not exactly what he needs, something very near to it in one or other of the many solutions presented in Part II. The author does not claim to give all the methods which have been used for measuring conductivity; but we think a reference might have been made to Yamagawa's experiments, in which a sphere of stone was subjected to a periodic surface variation by alternate immersions in boiling water and melting ice. The results are certainly of a higher order of accuracy than those of Ayrton and Perry with the cooling sphere.

Sechs Vorträge über das Thermodynamische Potential. By J. J. VAN LAAR. Friedrich Vieweg und Sohn. Braunschweig, 1906. These lectures exemplify the use of the thermodynamic potential in the treatment of the outstanding problems of solution and saturation. They are prefaced by two polemical lectures in which the author criticises in a lively manner the worshippers of the osmotic pressure.

The Scientific Papers of J. WILLARD GIBBS. In Two Volumes. Longmans, Green & Co. 1906.

These volumes contain in attractive form the important contributions made to scientific journals and transactions by the late Professor Willard Gibbs, of Yale University. Undoubtedly his greatest work was in connexion with thermodynamics. His first paper on Graphical Methods appeared in 1873; and in 1876 and 1878 appeared in two memoirs the remarkable and truly original discussion of the equilibrium of heterogeneous substances. It is a great advantage to have these papers together and easily accessible. The thermodynamic papers fill the first and larger volume. In the second volume the contents are of varied character; but probably the most interesting sections are those which concern vector analysis and multiple algebras. Here the mathematician will find some food for thought. The first volume is prefaced with a biographical sketch by H. A. Bumstead, and a complete bibliography. The portrait which forms the frontispiece shows a clear cut intellectual face of the best New England type.

A Compendium of Spherical Astronomy. By SIMON NEWCOMB. The Macmillan Company, New York, and Macmillan & Co., London. 1906.

THE precise nature of the present volume is indicated by the continuation of the title,—"with its application to the determination and reduction of positions of the fixed stars." It is, as we learn from the preface, the first of a series, intended not only

for the student but for the working astronomer. It is from the point of view of the student that we consider the book here. The three opening chapters form Part I., and are devoted to preliminary questions such as the meaning and use of small quantities, interpolation, and determination of probable errors. Chapters IV. to IX., which constitute Part II., deal with the fundamental principles of spherical astronomy, and discuss in order spherical coordinates, measurement of time, parallax and figure of the earth, aberration, astronomical refraction, and precession and nutation. Having thus laid the foundations strong and sure, Prof. Newcomb proceeds to consider in the four remaining chapters which make up Part III. the reduction and determination of positions of the fixed stars. The value of this part is enhanced by the fact that real examples are worked out in full as illustrations of the methods described. At the end of each chapter is appended a set of historic notes which give with great conciseness the important lines of development. Where all is so admirable it is difficult to pick out particular points for special reference. The discussion of astronomical refraction seems, however, to merit special notice. The treatment is fresh, and should be read by all mathematical and physical students, even although they should have no intention to pursue astronomical studies further.

#### Meteorologische Optik. Von J. M. PERNTER. III. Abschnitt. Wien und Leipzig: W. Braumüller. 1906. Pp. 346.

In this volume the author continues his exhaustive account of meteorological optics. The first section of this monumental work appeared in 1902, and was soon followed by Section II., which appeared later in the same year. Both were noticed briefly in these columns. Section III., now under review, deals with phenomena produced by particles not always present in the atmosphere—ice crystals and water-drops of clouds and rain. This section of the work is divided into three chapters, the division being based on the particular effects to which the phenomena in question are due. Thus, Chapter I., which fills the greater part of the volume, deals with phenomena caused by refraction and reflexion - halos and parhelia. Numerous illustrations and accounts of some very remarkable instances of such appearances are given, and a very thorough classification of snow crystals, with numerous plates illustrating their different forms, is incorporated in this chapter. Chapter II. treats of phenomena due solely to diffraction-coronæ and similar effects, while Chapter III. is devoted to rainbows. The same thorough method of treatment is followed by the author throughout. We first have a descriptive account of the appearances dealt with, then a detailed theoretical explanation. and lastly an account of experimental arrangements which enable us to reproduce the effects dealt with, and to supply a test of the soundness of the theoretical explanations. To the student of meteorological optics this work will be full of interest.

Two New Worlds. I. The Infra-World. II. The Supra-World. By E. E. FOURNIER D'ALBE, B.Sc. London: Longmans, Green, & Co. 1907. Pp. vii + 159.

This intensely interesting and strikingly bold essay on the relativity of time and space, and on man's position in the universe, deserves to be widely read. "The main thesis of this work"—to quote from the author's Preface—"is that a universe constructed on a pattern not widely different from ours is encountered on a definite and measurable scale of smallness, and another on a correspondingly larger scale. To these universes I give the names Infra-World and Supra-World respectively." Our "atoms" are the suns and stars of the "Infra-World," while our "electrons" represent its planets. An electron may, for aught we knew to the contrary, be of as complex a structure as our planet, and may be teeming with life. Lengths and times in this "Infra-World" are reduced in the same ratio of about 1022 to 1, and absolute velocities are of the same order as those in our world. Similarly, our planets form the electrons of the "Supra-World," our solar systems its atoms; the ratio of times and magnitudes being again 10<sup>22</sup> to 1, and absolute velocities being as before of the same order as ours. Our faculties enable us to perceive only three links of the chain of universes. The remaining links are concealed from us, and are (to us) at present non-material.

The author writes in an interesting way, and the concluding chapters of the book contain many stirring passages. Even to those who may not be prepared to agree with the author's conclusions,

the book will be an intellectual treat.

## LIV. Proceedings of Learned Societies.

GEOLOGICAL SOCIETY.

[Continued from p. 204.]

December 4th, 1907.—Sir Archibald Geikie, K.C.B., D.C.L., Sc.D., Sec. R.S., President, in the Chair.

THE following communications were read:—

- 1. 'The Faunal Succession in the Carboniferous Limestone (Upper Avonian) of the Midland Area (North Derbyshire and North Staffordshire).' By Thomas Franklin Sibly, B.Sc., F.G.S.
- 2. 'Brachiopod Homœomorphy: "Spirifer glaber".' By S. S. Buckman, F.G.S.

December 18th.—Sir Archibald Geikie, K.C.B., D.C.L., Sc.D., Sec.R.S., President, in the Chair.

The following communications were read:—

1. 'Some Recent Discoveries of Palæolithic Implements.' By Sir John Evans, K.C.B., D.C.L., LL.D., F.R.S., For.Sec.G.S.

2. 'On a Deep Channel of Drift at Hitchin (Hertfordshire).' By William Hill, F.G.S.

Evidence is given, from nine borings running along a line slightly west of north from Langley through Hitchin, of the existence of a channel of considerable depth, now filled with Drift, occupying the centre of an old valley in the Chalk-escarpment, which may be called the Hitchin Valley. For the first 3 miles it appears to be contained within narrow limits, persistent ridges of Chalk occurring on each side, and it might almost be compared to a Chalk-combe. At Hitchin, after passing between two Chalkknolls, its confines become less clear, and there seems to be some evidence of broadening as it emerges on to the Lower Chalk-plain and leaves the higher ground of the main Chalk-escarpment. The greatest depth to which the channel has been proved is at a boring in Hitchin, where the Gault was reached beneath Drift at a depth of 68 feet below sea-level. That the channel flowed northwards and belonged to a 'subsequent' stream seems to be proved by the fact that at Braybury End, the only place where a southerly stream could pass, the space between bare Chalk-exposures is but 450 yards. and in about the middle of the space Chalk has been reached within 50 feet of the surface (that is, about 200 feet above sea-level) in a well dug a few years back. The channel must be older than the Chalky Boulder-Clay, which still partly fills it as far south as Langley, and may have blocked it to the southward and given rise to the features now presented in the drainage on the northern slope of the escarpment. But the author is inclined to suggest that either glacier-ice or bay-ice must have played no unimportant part in damming up the old valley. The author suggests the existence of another channel, in this case draining southwards, buried under the broad area of Boulder-Clay and gravel which lies immediately south of Stevenage and to the north as far as Letchworth and Wilbury Hill. But a narrow space of bare Chalk, at an elevation of 240 feet O.D. connecting large areas east and west of it, precludes the occurrence of a channel farther north than Letchworth.

January 8th, 1908.—Sir Archibald Geikie, K.C.B., D.C.L., Sc.D., Sec.R.S., President, in the Chair.

The following communications were read :-

1. 'Chronology of the Glacial Epoch in North America.' By Prof. George Frederick Wright, F.G.S.A.

In the case of Plum Creek, Lorain County (Ohio), the study of the activity of the stream and of the amount of work which it has done since a certain stage of the Glacial Epoch, has yielded important results. This stream began the erosion of its trough when the temporary lake, held up in front of the ice, was maintained for a considerable period at the level of its Fort-Wayne outlet; it has

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never had anything more resistant than Till to act upon. From a given section, 5000 feet long, it has excavated 34 million cubic feet of Boulder-Clay, removing it from exposed banks 1600 feet long. Twelve years' erosion of a 500-foot length of a part of the trough of the stream under observation, and from banks 1000 feet long, gives a rate of 8450 cubic feet per annum. Therefore, the removal of 34 million cubic feet from the 5000-foot section would give a period of 2505 years. Considerations tending to lengthen the estimate are the former forestation of the area and the increased gradient in the artificial cut-off. Those tending to shorten the estimate are the present wider flood-plain, the time taken for forests

to grow, and the probably greater former water-flow.

The erosion of the Niagara Gorge began considerably later than that of Plum Creek, and probably dates from midway between the disappearance of the ice from Northern Ohio and from Quebec. If conditions have been uniform, the age of the Gorge would be 7000 years. As the Niagara Limestone is thinner at the mouth of the Gorge, and the Clinton Limestone has dipped out of sight at the Whirlpool, there is nothing in the stratigraphy to indicate a slower recession in the past than in the present. Moreover, nearly one-third of the erosion has been accomplished by two pre-Glacial streams, one from the south and a smaller one from the north. Therefore, the author concludes with considerable confidence that the Gorge is less than 10,000 years old, and that the ice of the Glacial Epoch continued down to that time, to such an extent over the lower St. Lawrence Valley and Central New York that it obstructed the entire eastern drainage of the Great Lakes.

There is nothing which would lead to a longer estimate of the time which has elapsed since the Kansan stage of the Glacial Epoch than that approved by Prof. Calvin of Iowa, and agreed to by Prof. Winchell. These assume 8000 years as the limit for post-Glacial time, and that a multiple of this by 20, amounting to 160,000, would carry us back to Kansan time. This, however, would still leave as long a period still earlier, for the advance of the ice. The author's impression is that the whole epoch may well have been

compassed within 200,000 years.

2. 'On the Application of Quantitative Methods to the Study of the Structure and History of Rocks.' By Henry Clifton Sorby, LL.D., F.R.S., F.L.S., F.G.S.

The knowledge of the final velocities of material subsiding in water is of fundamental importance; but the relation between size of particles and velocity is complex, and perhaps may be partly explained by a thin, adherent film of water. The angle of rest in the case of sand-grains of varying size and quality enables us to ascertain approximately the velocity of current necessary to keep such sand drifting, and that needed to move it when at rest. The comparison of this angle with that observed in sedimentary rocks

made of similar materials may be used to determine the amount of vertical contraction of rocks since deposition, the average in cases studied in Tertiary and Secondary rocks being from 100 to 57. In studying the drifting of sand along the bottom by currents (on which the author experimented in a small stream many years ago), the results are found to vary, according to whether the water is depositing sand as well as drifting it, and according to whether ripples are or are not being formed on the bottom. The velocity of a current can be determined approximately in feet per second for different kinds The connexion between the structure of 'ripple-drift' and time is discussed; and an equation is given, from which the rate of deposit in inches per minute can be deduced. The connexion between the structure of a deposit and depth of water is found to be difficult to study quantitatively. From the occurrence of 'drift-bedding' the depth of water may probably be determined to within a few feet, and on this being applied to particular rocks some interesting results come out, including the separation of sandstones into several different groups. The deposition of fine deposits, like clay, is a most complex subject, varying according to the amount of mud present in the water, and according to whether the grains subside separately or cohere together. When no pressure is applied, even when no further contraction takes place on standing for a year, the amount of water included in the deposited clay may be 80 per cent., and, when dry, the minute empty spaces may still amount to 32 per cent. This leads to the conclusion that many of the older rocks must now be only 20 per cent, of their original thickness. In many cases there is produced by a gentle current a minute laminar structure from which probably the rate of deposition may be learned approximately, a common rate in the older rocks being from 9 to 18 inches per hour. But complex and difficult experiments are very desirable on this question. The rocks classed as clays differ very much in structure, and must have been formed under different conditions.

Applying these conclusions to various rocks, the author shows that in the green slates of Langdale there is good evidence that the volcanic eruptions sometimes occurred within a few weeks of one another, and at other times at more distant intervals. Now and then there were bottom-currents, probably due to volcanic disturbances, gradually rising to a rate of about 1 foot per second and gradually subsiding, the entire period being a few minutes, and deposition taking place in different cases at from  $\frac{1}{10}$  to 2 inches per minute. There is also good evidence that, when deposited, part of the rock was analogous to fine, loose sand, and part to semi-liquid mud. In the Coal-Measure sandstones deposition at the rate of 1 inch per minute was common, with intervals of little or no deposit.

The volume of invisible cavities in rocks varies from 49 per cent. in some recent rocks, to nearly 0 in the ancient slates. The packing of grains is discussed mathematically and experimentally,

the latter with round and flattened shot; and experiments with sand of various qualities, rapidly deposited and also when well shaken, show a good agreement with calculation. The methods of determining the volume of minute cavities in rocks are given, followed by a number of examples from recent and older deposits. It is found that in some limestones the cavities have been reduced by pressure to close on the mathematical minimum, whereas in others, even of Silurian age, the cavities were filled with carbonate of lime, introduced from without, not long after deposition. Some oolites have had their cavities filled in a similar manner; in others most of the material of the original grain has been removed, and the present solidity is due to the filling-up of the original cavities mainly by internal segregation. Among fine-grained rocks the Chalk probably was originally a sort of semi-liquid with fully 70 per cent, of its volume water, and in its present state is about 45 per cent, of its original thickness; the thickness of some clays must have diminished still more; while the amount of minute cavities in rocks with slaty cleavage is so small, that sometimes they are nearly solid.

By the measurement of green spots in slates it can be deduced that the rock before cleavage was somewhat more consolidated than rocks of the Coal-Measures now are, and was then greatly compressed and the minute cavities almost completely squeezed up. The development of 'slip-surfaces' in cleaved rocks is very great, and furnishes an additional proof that the cleavage is of mechanical

origin. 'Pressure-solution' is also dealt with.

In conclusion, the author discusses the volume of minute cavities in clay-rocks and their analogues of various ages, and shows that there is a distinct relation between it and the probable pressure to which the rocks have been exposed. Tables are given of the pressures so calculated for rocks of various geological ages, the volume of empty spaces decreasing in older rocks from the 32 per cent. existing in recent clays. In the Moffat rocks, with very little or no slaty cleavage, the pressure is calculated at about 7 tons to the square inch, while the Welsh slates, with very perfect cleavage, indicate a pressure of about 120 tons to the square inch.

January 22nd.—Sir Archibald Geikie, K.C.B., D.C.L., Sc.D., Sec.R.S., President, in the Chair.

The following communications were read:—

1. 'The Origin of the Pillow-Lava near Port Isaac in Cornwall.' By Clement Reid, F.R.S., F.L.S., F.G.S., and Henry Dewey, F.G.S.

The Upper Devonian strata around Port Isaac consist of marine slates, in which occurs a sheet of pillow-lava over 200 feet in

thickness. The pillows measure usually from 2 to 5 feet in diameter, but range up to 8 feet; masses under 1 foot are rare. The individual pillows are quite disconnected, although moulded on one another and adherent where they touch. Where three pillows approached there was an angular vacant space, subsequently filled with calcite, which is often altered into chert. Their mutual relations seem to prove that they were soft when deposited, but not sufficiently soft to squeeze into corners.

Each pillow shows internally a central vacant space or very open sponge, often as much as 2 feet in length. This is succeeded by a thick shell of exceptionally vesicular lava, which is followed by an outer shell of banded, more or less vesicular rock. The whole mass

is so vesicular that it must have been very light.

If this lava were subaërial, the lightness would not help us to explain the origin of the isolated pillows; but the intimate association with fine-grained marine strata shows that it was probably submarine. On calculating the proportion of cavity to rock in two of the pillows, the authors find that the specific gravity of the whole mass must have been very low, not greatly exceeding that of seawater. The lava seems to have been blown out into thick-walled bubbles, kept from touching each other by the escaping steam. The whole mass was for a short time in the spheroidal state, and, although composed of a multitude of large plastic spheres, the sheet could flow like a liquid. This eruption seems to have been analogous to that of Mont Pelé, described by Dr. Tempest Anderson & Dr. Flett, except that it was submarine instead of subaërial.

2. 'On the Subdivision of the Chalk at Trimmingham (Norfolk).' By Reginald Marr Brydone, F.G.S.

The object of this communication is to lay before the Society a sketch-map showing the geographical distribution of the subdivisions, with a brief account of their distinguishing features. Practically the whole of the Chalk exposed on the foreshore comes under two main divisions—one composed of (a) Sponge-beds, very largely yellow, 12 feet, resting on 8 feet of White Chalk; (b) White Chalk without Ostrea lunata, about 9 feet thick; (c) White Chalk containing O. lunata, 20 feet; and the other composed of (a) Grev Chalk, about 12 feet thick; succeeded by (b) White Chalk with Ostrea lunata, about 20 feet; (c) White Chalk without O. lunata, about 8 feet; (d) White Chalk with O. lunata, about 10 feet; and (e) Grey Chalk, about 25 feet. There is no evidence as to the relative positions of these two main divisions. The author seeks to justify his adoption of Terebratulina gracilis and T. Gisei as the zone-fossils of the Trimmingham Chalk, in opposition to the proposal to adopt Ostrea lunata as the zone-fossil. Other important species are Pentacrinus Agassizi, P. Bronni, and Echinoconus Orbignyanus. The author still adheres to his view that these masses of Chalk

can only be in situ and must have once formed part of a large continuous mass, and that the bulk of this mass must have lain to seawards of the present coast-line.

February 5th.—Sir Archibald Geikie, K.C.B., D.C.L., Sc.D., Scc.R.S., President, in the Chair.

The following communications were read:-

1. 'On Antigorite and the Val Antigorio, with Notes on other Serpentines containing that Mineral.' By Prof. T. G. Bonney, Sc.D., LL.D., F.R.S., F.G.S.

It is by no means certain, as the author ascertained after his joint paper with Miss Raisin, published in 1905, that the first-described specimen of antigorite was really found in the Val Antigorio. So last summer he visited that valley, in company with the Rev. E. Hill, and after an examination, of which he gives an account, came to the conclusion that the rock most probably does not occur there in situ, though it is found in pebbles, etc. from tributaries.

He next describes other specimens of antigorite-serpentine, examined since 1905: some from New Zealand, kindly sent to him by Dr. J. M. Bell, and others obtained in the Saasthal, especially from the Langefluh; giving further particulars about specimens in the National Collection at South Kensington and in the University Collection at Cambridge.

He then discusses the origin of the mineral. Pressure is apparently essential; certainly it can be formed from augite, and, though he has not discovered residual olivine in his own rather numerous specimens, or typical antigorite in Alpine bastite-serpentines, he finds indirect evidence of its coming from this mineral, proofs of which are given by F. Becke, M. Preiswerk, and J. M. Bell. If, however, we suppose the former existence of two types of peridotite in the Alps, as at the Lizard and in the Vosges, and pressure sometimes to have preceded, sometimes to have followed serpentinization, we can account for the apparent conflict of evidence.

2. 'The St. David's-Head "Rock-Series" (Pembrokeshire).' By James Vincent Elsden, B.Sc., F.G.S.

The St. David's-Head and Carn-Llidi intrusions are of complex composition, ranging from a basic biotite-norite to an acid quartz-enstatite-diorite, and finally to soda-aplite. Throughout all the types, except the last, there is a high magnesia-percentage. The extreme types sometimes pass abruptly one into the other, and at other times they are mixed in various proportions. They do not represent a composite intrusion, but simultaneous intrusions of an

imperfectly-mixed magma. There is no evidence of differentiation in situ, but the facts suggest a common origin from a differentiated magma-basin. The aplite-veins may represent the most acid phase

of the differentiated magma.

Petrographically the rocks are of considerable interest, as exhibiting types not very commonly occurring in the British They also afford unusual facilities for the study of both rhombic and monoclinic pyroxenes, and appear to throw light upon the origin of the sahlite-striation of the latter. Rhombic pyroxene generally crystallized earlier than the monoclinic pyroxene, but sometimes these relations are reversed, and often the two forms are crystallographically intergrown, sometimes as twins. There are two distinct varieties of augite, distinguished by the presence or absence of a basal striation. The relation of these two types lends support to the perthitic theory, that there is an ultra-microscopic crystallographic intergrowth of rhombic and monoclinic pyroxene. The probable age of the intrusions is not greater than that of the earth-movements which folded the Arenig Shales in this district. The observations recorded in the paper seem to point to the conclusion that acid streaks and cores in basic igneous rocks may not always be due to differentiation in situ.

February 19th.—Sir Archibald Geikie, K.C.B., D.C.L., Sc.D., Sc.R.S., President, in the Chair.

The following communications were read:-

1. 'The Two Earth-Movements of Colonsay.' By William Bourke Wright, B.A., F.G.S.

The supposed Torridonian rocks of Colonsay exhibit in their folding and cleavage the effects of two movements analogous in their results to those proved by Mr. Clough in the Cowal district of Argyll. Not only the planes of the first or slaty cleavage, but also the quartz-veins formed along them have been folded by the second movement, and may be observed to be crossed at considerable angles by the cleavage produced during this second movement. An extensive series of lamprophyre-dykes, obviously later than the first cleavage, are found to be folded and cleaved by the second movement. Moreover, some of these dykes traverse and are chilled against a mass of syenite, which can also be proved to be later than the first cleavage. The distinctness of these two movements is, therefore, considered to be completely established. The second cleavage being of the nature of strain-slip, its development along the axial planes of the folds is of interest and is briefly discussed.

2. 'Notes on the River Wey.' By Henry Bury, M.A, F.L.S., F.G.S.

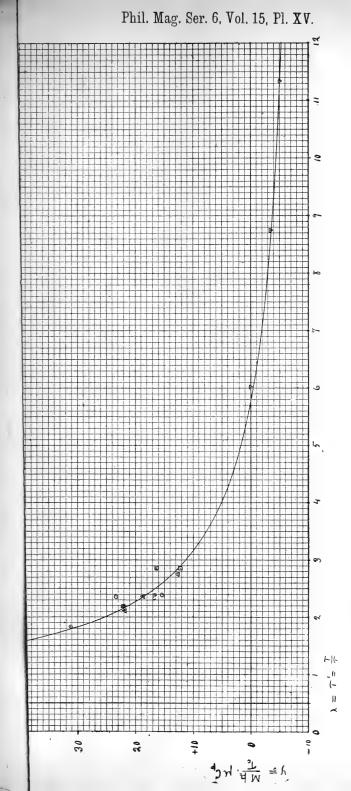
The part of the River Wey within the Wealden area is divided

into six sections:—(1) The consequent river cutting the Chalk at Guildford; (2) the subsequent stream coming in from the east at Shalford; (3) the western subsequent stream parallel to the Hog's Back; (4) the continuation of the last westward (the Tilford River). rising at Selborne and receiving many tributaries, including the Headley River, from between Blackdown and Hindhead; (5) the short obsequent section from Farnham to Tilford (the Waverley River); and (6) the portion above Farnham coming from Alton and beyond (the Farnham River). Part I deals with the relation of sections 6, 5, & 4 to the Blackwater. It is assumed that there was a consequent river coming down from Hindhead, flowing northwards along the 'Waverley River,' and joined by the Farnham; Tilford, and Seale rivers. This seems to have been the original head of the Blackwater. But subsequently capture took place by section 3 of the Wey, with the result that the Tilford River passed into the Wey basin, and section 5 was thus beheaded. The development of an obsequent stream near the course of the last eventually tapped the Farnham River, but not the Seale.

Part II deals with the Palæolithic Gravels of Farnham. Their height and distribution is discussed, with a view of determining the river which originated the gravels. The ridges constituted by the gravel drop to a lower platform along the Waverley River: this is regarded as the left bank of the consequent valley before that was beheaded. If this were the case, the gravel would have been formed by the Farnham River while still tributary to the Blackwater. At this time, too, probably the Headley tributary drained into the Farnham, and not the Tilford River, giving rise to the south-western

portion of Alice Holt.

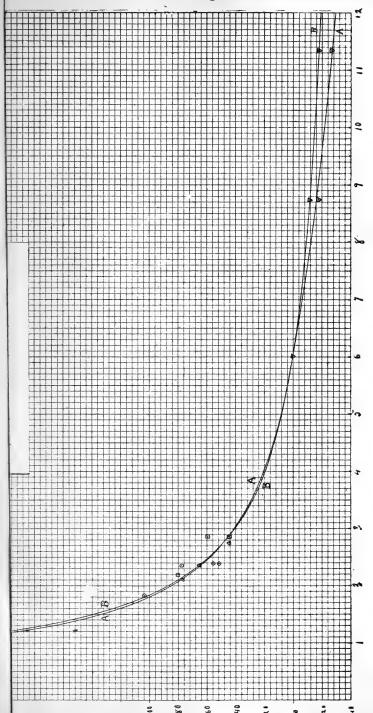
Part III deals with the Farnham branch of the Wey and the Alton district, which is remarkable in that there is a complicated series of Chalk-valleys, which spread over some 50 square miles of country and discharge their waters into the Wealden area. possible explanation is that this portion originally drained into the Whitewater over the present col of Golden Pot. In discussing this explanation, it appears that the Tisted tributary has the characters of a consequent stream; but there is no very good evidence, except alignment, of the former connexion of the two basins. On the other hand, the Farnham River rather appears to have originated in a Chalk-surface than in Wealden beds; and thus it and its tributaries may have been developed on the Chalk portion of the peneplain of the Weald. Thus the Farnham stream appears to present a case of the conversion of a Chalk-valley into a Wealden one in its lower part, while in the Caker stream the reverse is the case, and it is the upper part of the stream that has entered Wealden beds.







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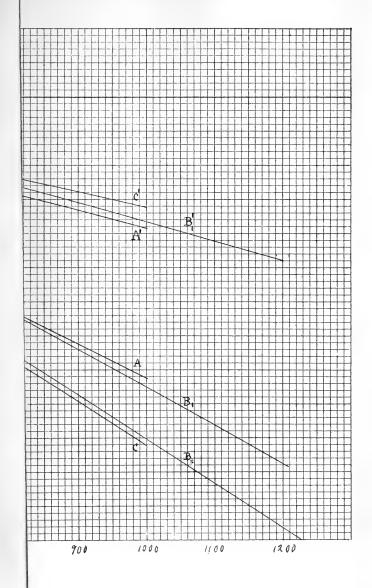




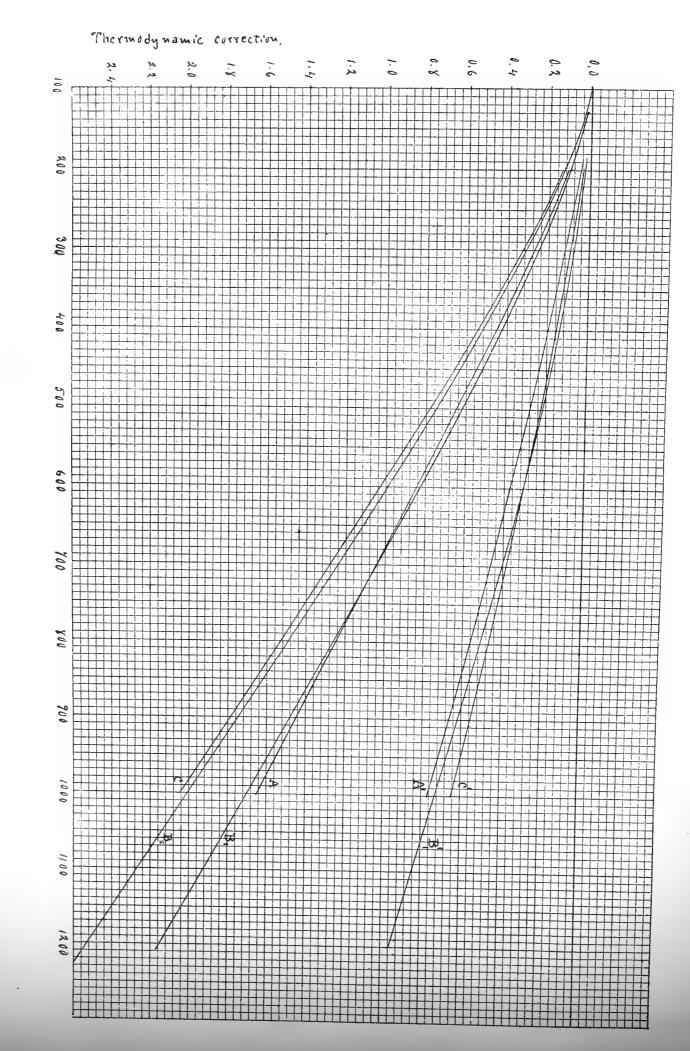
Ser. 6, Vol. 15, Pl.



Phil. Mag. Ser. 6, Vol. 15, Pl. XVII.









THE

## LONDON, EDINBURGH, AND DUBLIN

# PHILOSOPHICAL MAGAZINE

AND

# JOURNAL OF SCIENCE.

[SIXTH SERIES.]

MAY 1908.

LV. The Resonance Spectra of Sodium Vapour. By R. W. Wood, Professor of Experimental Physics, Johns Hopkins University\*.

#### [Plates XVIII. & XIX.]

THE vapour of sodium, obtained by heating the metal in a highly exhausted steel tube to a temperature of about a highly exhausted steel tube to a temperature of about 400 degrees, yields an absorption spectrum of great complexity. In addition to the D lines and the other lines (ultraviolet) of the principal series, which come out reversed, we find the entire visible spectrum, with the exception of a very narrow region in the yellow, filled with fine and sharp absorption-lines. This we shall call the channelled absorption spectrum, and we find it divided into two distinct regions, one extending from wave-length 4500 to 5700, and the other extending from about 5800 to the extreme limit of the red. It is probable that it extends out as far into the infra-red as 10 or  $12 \mu$ , for recent investigations by the writer, in collaboration with Professor A. Trowbridge of Princeton, have shown that the vapour exhibits heavy absorption in this region, though the bolometer strip was not narrow enough to resolve the lines. This remarkable absorption spectrum was investigated by the writer in collaboration with J. H. Moore a number of years ago; but the precision which is now being obtained in the work upon the fluorescence of the vapour has made a

<sup>\*</sup> Communicated by the Author.

still more accurate study of it advisable, and this work has been carried on by Mr. Clinkscales, one of my students, during the past year. Photographs taken with the 21-foot grating in the second-order spectrum, show that it is even more complicated than was originally believed. We find, on the average, from 60 to 70 absorption-lines within a space only 12 Ång. units in width; in other words, as many as 30 lines in a region no wider than the distance between the D lines. This means that in the blue-green channelled absorption spectrum, which is about 1200 A.E. in width, there are roughly speaking about 6000 absorption-lines. Taken collectively these lines form themselves into a number of groups, which resemble the groups seen in the absorption spectra of iodine and bromine, and in certain banded emission

spectra.

A small portion of the absorption spectrum of sodium vapour in vacuo, taken with the 21-foot grating in the second-order spectrum by Mr. Clinkscales, is reproduced on Pl. XIX. figs. 4 & 5. The originals have been enlarged about six-fold, and the portions reproduced are thus on a somewhat larger scale than Rowland's large map of the solar spectrum. Each of the strips reproduced is a little less than 20 Ångström units in width, or considerably less than the distance between the series lines in the resonance spectra, the spacings of which vary from 36 to 38 units. The strong iron lines in this region appear on the plates for comparison. absorption-lines are seen to be separated by distances which in some cases are less than 0.15 unit in width. When the resonance spectra have been photographed with the 12-foot grating, an immense amount of information can be obtained by comparing the spectrograms with this magnificent map of the absorption spectrum. This map will enable us to determine whether a given exciting line strikes an absorptionline exactly, or falls midway between two. It must be distinctly understood that the spectrum reproduced is a positive and not a negative of the absorption spectrum. It resembles a bright-line emission spectrum so closely, that I deem it of importance to draw attention to this fact. It is most remarkable that we can absorb portions of a continuous spectrum and leave regions not much over 0.05 or 0.1 of an Angström unit in width, and it would be interesting to examine this residual light, after transmission through the vapour with a Fabry and Perot interferometer. A discussion of this remarkable transmitted spectrum from the point of view of the pulse theory of white light should prove interesting, for the light transmitted appears to be as homogeneous as the light in the spectrum of the iron arc.

To attempt to unravel this spectrum, or find any regularities in it by the usual means, is quite out of the question, for the lines are so numerous and so close together that we could pick out series that would conform to any law that we might choose to invent.

As I have shown in a previous paper, however, we possess a very beautiful experimental method of analysing the spectrum, and of determining just which lines belong together; a method, moreover, which may in time yield results which will enable the theoretical physicists to tell us the exact nature of the piece of machinery which we call the sodium molecule.

If we illuminate the vapour with a powerful beam of white light, it becomes strongly fluorescent, emitting a spectrum which I now believe to be the exact counterpart of the absorption spectrum. During the earlier part of the work, before the methods and apparatus had been perfected to the high degree which they have now reached, it was believed that comparatively few of the absorption-lines gave rise to fluorescence, as the fluorescence spectrum could not be photographed with the high dispersion which is now employed. This fluorescent spectrum is obviously of little help to us, for it is quite as complicated as the absorption spectrum. If, however, we throw monochromatic light into the vapour, instead of white light, we observe a very remarkable phenomenon. We now have series of bright lines spaced at very nearly equal intervals along a normal spectrum, and separated by a distance equal to about 37 Angström units. Various series of lines with varying distribution of intensity can be brought out by changing the wave-length of the exciting light. In every case, light of the same wavelength as that of the exciting light is emitted by the vapour, and in addition a large number of other frequencies, which bear a definite relation to each other. In the absence of the exciting light the vapour is non-luminous, that is the electrons, which we may perhaps regard as revolving in concentric rings, do not radiate any energy. The passage of an intense beam of monochromatic radiation through the medium disturbs this non-radiating system in some way, and causes it to emit a series of bright spectrum-lines. phenomenon can of course be classed under fluorescence if we choose, but as we appear to be dealing with a much more tangible phenomenon than is usually the case, and as these 2 R 2

spectra are radically different from spectra excited by any other means, I propose that they be named Resonance spectra, since they are without doubt excited by the resonance of one or more of the electrons of the system when monochromatic

radiation plays upon it.

During the past year much additional information has been gathered regarding these remarkable spectra, and though the work is by no means completed at the present time, it seems advisable to place on record the results obtained thus far, in view of the fact that theoretical papers (notably those by G. A. Schott) are appearing from time to time on the nature of the radiation emitted by electron systems.

I have already shown that the D lines are present in the emission spectrum when the vapour is excited by light of the same wave-length. This fact is of interest in connexion with statements recently made by some writers that the D lines are never present unless oxidation is going on, and in the air-tight steel tubes, highly exhausted and repeatedly washed out by the hydrogen evolved by the sodium, it is

difficult to see how any oxygen can be present.

The very remarkable fact has now been established that the D lines can be caused to appear in the emission spectrum by stimulating the vapour with a very intense beam of bluegreen light, from which all yellow light has been completely eliminated. This proves that the mechanism which produces the principal series is a part of, or connected in some way with, that very complicated piece of machinery which gives rise to the channelled absorption spectrum with its thousands of lines.

The second point of interest is the discovery of series of equidistant lines in the red fluorescent spectrum, excited by monochromatic red light, the photographic recording of which has been made possible by the panchromatic plates recently placed on the market by Wratten and

Wainwright.

The spectrum emitted when the vapour is stimulated by white light has been photographed under more favourable conditions with a large grating, and has been found to possess much more structure than was at first supposed, especially in the yellow-green region, where very little fine detail could be made out in the earlier photographs.

The magnetic-rotation spectrum has been studied with a view of determining whether the rotatory power is positive or negative for the different electrons. The results obtained in the red region of the spectrum have been already

published \*.

The resonance spectra obtained by stimulating the vapour with the radiations from the cadmium and zinc quartz arclamps have been photographed with a large grating, and the wave-lengths of the bright lines which form the series have been determined to within a tenth of an Angström unit, a tremendous step in advance over the work recorded in the earlier paper, in which we could not be sure of the wave-

lengths to within less than about 2 Ang. units.

Many new sources of monochromatic light have been used, and the prism spectrograph improved by the addition of a new long-focus photographic objective by Cooke. The resonance spectra described in the previous paper have been photographed over again with this improved apparatus, and we now know the wave-lengths of the lines to within a little less than one unit. During the present year they are being photographed over again with a 12-foot concave grating with a collimating lens of six feet focal length. This work, which will take an enormous amount of patience, is being carried on in collaboration with Mr. Felix E. Hackett. Fellow of the Royal University of Dublin.

Familiarity with the preceding paper above referred to will be presupposed in presenting the more recent results, as the details and methods have been already fully described. A few improvements have been made in the apparatus. Owing to the long exposures it has been found necessary to put a heating-coil and thermostat in the large three-prism spectrograph. This keeps the temperature constant to within a tenth of a degree, and improves the definition in no small degree. The telescope-lens has been removed and replaced by a Cooke photographic objective of  $3\frac{1}{2}$  inches aperture and 40 inches focus, which was made to order. This lens was corrected so as to be as nearly as possible achromatic for the spectrum range 4500-5700, within which the resonance spectra, which are being studied, fall. It also gives fair definition over the range of the entire visible spectrum. The wet cotton jackets on the sodium tube have been replaced by tightly wound coils of lead pipe (5 mms. diameter) through which a current of cold water circulates. In working with open air arcs much difficulty was experienced from the wandering of the arc over the surface of the electrodes. The image of the arc on this account moved

<sup>\* &</sup>quot;On the existence of Positive Electrons in the Sodium Atom," Phil. Mag. February 1908.

about over the aperture in the drum-retort of the sodium tube. The image of the carbons gave some trouble as well, exciting the complete fluorescence spectrum. Both troubles were obviated by focusing the arc on a small round hole in a screen by means of a large double-convex lens, and then throwing an image of the aperture into the sodium retort by means of a second lens. In this way it was possible to keep the white light away from the sodium vapour, and correct for the shifting of the arc by moving the lamp from side to side. As exposures of seven or eight hours are often necessary, it will be readily seen that the care of the arc is no light labour. A magnetic field was tried to keep the arc in a fixed position, but nothing appeared to be gained by this expedient.

The spectra excited by the radiations from the cadmium and zinc arcs in exhausted quartz tubes were photographed with a large plane grating in combination with the Cooke lens, and as the wave-lengths of the resonance spectra excited in these two cases have been determined with considerable accuracy, we will discuss them first. In each case the iron-spectrum was photographed in contact with the

resonance spectrum.

## Cadmium Excitation.

The wave-lengths of the lines in the resonance spectra excited by the monochromatic radiations from a cadmium-vapour lamp have been determined to within one or two tenths of an Ångström unit. In the previous paper I showed that stimulation of the vapour with the radiation of wavelength 4800 caused it to emit a series of bright lines spaced at very nearly equal intervals along a normal spectrum.

Whether the lines are in reality spaced at equal distances is a matter of considerable importance, since theoretical treatments of the radiation emitted by electron systems disturbed in various ways can only be verified by the test of experiment. Prof. Larmor has pointed out to me in a letter that a non-radiating system of electrons in steady orbital motion, when disturbed by the absorption of a radiation corresponding in frequency to the frequency of one of the electrons, should then emit radiations giving us a series of lines equally spaced along a normal spectrum. We must bear one fact in mind, however. The light emitted by the vapour is obliged to pass through a certain thickness of cooler vapour before reaching the spectroscope, and since the absorption-lines are very closely packed together, it is

quite possible that the apparent position of an emission-line of finite breadth may be to a slight extent modified by absorption. If, for example, there is a strong absorption-line on the violet side of and close to the emission-line, the centre of the emission-line will appear a little on the red side of its true position. Very slight departures from the law of equal spacing need not be regarded as fatal. A portion of one of the spectrograms is reproduced on Pl. XIX. fig. 2. Exciting line 5086 shows and 8 or 10 of the resonance lines—Comparison spectrum of iron.

The wave-lengths of the lines in the series excited by stimulation at wave-length 4800 are given in the following table, together with the wave-length differences.

λ.	λd	lifferences
4765.5	*******	34.5
4800 4835:8		55.8
40000	74.2	96.9
4000.0	$\frac{742}{2}$	=36.2
4908·2 4945·1	***************************************	36.9
4982.2	•••••	$37.1 \\ 37.5$
5019.7	***************************************	
•••••	$\frac{74.62}{2}$	=37.3
5094.27	************************	37.23
5131.5	***************************************	38.00
5169·5 5207·46	•••••	37.96
5245.2	C. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.	$37.74 \\ 37.56$
5282.76	**********************	38·63
5321.39	***************************************	38.03
5359.42		

Two only of the lines in the series are missing. In the previous investigation there were three that escaped detection. With longer exposure I feel confident that all would appear. It is clear that the lines are closer together in the region of shorter wave-lengths. The slight variations in the differences above the line 5019·7 are, in my opinion, due to the cause mentioned above. If we take the differences between five lines in the series instead of between two, we find the spacing averages remarkably constant. Starting at the top (longest line) of the series, the differences between each line and the fifth below it run as follows:—151·96, 151·89, 151·26, 150·93, 151·46, 149·8, 149·3, and 149·17.

The spectra are now being photographed with the 12-foot grating, and it is quite possible that still greater regularity will result. There seems to be no escape from the fact that the spacing widens slightly as we ascend the spectrum.

We will now consider the resonance spectrum excited by

the green cadmium-line 5086, which, as I showed in the previous paper, consists of a number of regularly spaced doublets.

The blue lines of the cadmium lamp were cut off by a screen of nitroso-dimethylaniline. In more recent work a screen composed of a concentrated solution of a neodymium salt has been found to work better.

The wave-lengths of the lines excited by the 5086 stimu-

lation are given in the following table:-

$ \begin{cases} 4969 \cdot 0 \ a \\ 4975 \cdot 0 \ b \\ 5007 \cdot 9 \ a \\ 5013 \cdot 6 \ b \\ 5046 \cdot 8 \ a \\ 5052 \cdot 7 \ b \\ 5086 \cdot 0 \ a \end{cases} $		1	) <sub>I</sub> fferen(	CES.	
l 5091·3 b f 5125·0 a	a.	b.	c.	đ.	€.
5130·3 b	38·9 39·0	38·6 39·1	40·9 38·0		37.1
5159·0 c	39.2	38.6	38.1		
∫ 5164·4 a	39.0	39:0	001		
\ 5169.5 b	39.4	39.2			
5195·2 d 5199·9 c	38.0				
5202·4 a					
5237.9 c					
52385 e					
5276.0 c	-				
5305·6 €					

In this table we see that in addition to the doublets which I have spoken of, and which are bracketed, there are a number of other lines. The lines which belong to the same series of equidistant lines are indicated by letters. We find in this case that as we approach the upper limit of the series, other lines appear on the short wave-length side of the line or lines at the upper end, a new series starting where the old one leaves off. This same thing occurs in many other instances, as in the resonance spectrum excited by the barium line 4934.

It is a little difficult to express in words exactly how these lines come in, and a much better idea can be gained by applying a pair of compasses to the chart and spacing off the series, and noting how the lines of the new series appear on the short wave-length side of the lines which are being spaced off.

I have given the differences between the wave-lengths of the lines of the different series, a, b, c, and e in a separate

table. The line d appears to be isolated.

### Zinc Excitation.

The wave-lengths in the resonance spectrum excited by the three blue zinc lines have been determined to within less than 0.2 A.E. Two negatives were made with the large grating and Cooke long-focus lens, one with an exceedingly narrow slit, which was used for the measurements, and one with a wider slit, which is reproduced on Pl. XVIII. fig. 2: the white-light fluorescence above, iron comparison between. On this Plate the lower end of the spectrum did not appear owing to the fact that a corner of a black cloth inside the spectrograph slipped down in front of the end of the plate. The reproduction gives a good idea of the sharpness of the lines in the resonance spectrum, although the exciting lines do not appear on the plate. It must be remembered too that this plate was made with what I have termed a wide slit.

The resonance spectrum contains a large number of series of equidistant lines, though the series are not as extended as in the case of the cadmium excitation and many others

which will be considered presently.

I have not, at the present time, photographed the spectra excited by the three lines separately, but by comparing the plate made with the grating with the one made in the earlier work, I have made a provisional assignment of the lines which I believe belong to the spectrum excited by the longest of the three zinc lines. These lines I have marked with a star in the Table of wave-lengths, and have designated with letters a, b, c, &c., the lines which appear to belong to the same series.

As many lines appear double in the present photographs which appeared as single lines in the earlier spectrograms, it will be understood that too much importance must not be attached to the present assignment of the lines. Many of the series appear to have missing lines, and an attempt is now being made to find them with longer exposures. Exposures of 8 or 10 hours were necessary with the quartz zinc lamp fed by a current of 5 amperes, and the lamps are of very little use after a run of 25 or 30 hours, owing to a black deposit (reduced silica probably) which forms on the inner surface of the tube.

The wave-lengths follow, together with the differences of wave-length of the lines which appear to belong to the same series. The exciting lines are underscored, and the relative intensities are roughly indicated by numerals, 10 meaning

very strong, and 1 very faint:—

4647.2 2	5168.8	1	5410.0	6*
4648.9 2	5181.1	1	5414.0	3
4655.3 2	5184.2	1	5418.4	1
4680.4 10	5186.8	6*b	5420.0	1
4684.5 2	5196∙∪	1 d	5421.8	6
4685.8 2	5215.3	2c	5423.3	6
4688.5 4	5220.6	1	5427.6	2
4700.1 1	5225.8	4*b	5432.2	2
4713.5 7	5232.0	3*d	5438.0	6
4714.4 7	5244.0	1	5440.3	1
4719.7 3	5248.7	1	5442.7	3d
4722:3 10	5252.8	1 * c	5443.9	5
	5253.7	2	5448.2	2
4746.5 2	5264.5	2*b	5451.5	5
4747.5 3	5268.0	$\overline{1} d$	5454.4	8
4748.6 5	5273.0	1	5457.3	3
4753.8 1	5277.6	1	5458.8	1
4755.8 6	5290.2	9 * 0	5465.1	2
4774.7  2*a	5300.0	1 *	5471.7	4
4776.0 2	5303.1	2 * b, d	5475.8	2
4783.1 1	5305.6	2	5478.0	3d
$4810.7 \ 10*a$	5307.5	1	5482.6	4
4813.4 1	5313.7	2	5484.1	5
4818.2 1	5315.8	1	5486.9	7
4822.2 2	5321.1	3	5490.0	3
4823.6 2	5327.0	3	5494.1	1
4845.4 4	5328.5	6*c	5496.2	3
4847.2  4*a	5338.1	8*d	5502.0	2
4853.4 1	5350.5	2	5505.6	2
4858.5 1	5351.6	4	5512.5	1 d
4883·6 2 * a	5356.5	1	5512.9	2
4914.8 1 *	5366.0	1 c	5516.1	3
4955·8 1 a	5370.0	1	5519.3	2
4958·7 2 * b	5373.5	8*d	5521.7	2
4984.6 1	5375.9	5	5526.7	1
5029·2 3 a	5379.2	1	5532.6	1
5034.1  2*b	5386.1	2	5535.2	2
5055.4 3	5387.4	5	5538.0	2
5065·1 1 a	5390.2	2	5547.8	1
$5072.3 \ 2 * b$	5391.9	3	5557.6	4
5103.4 2	5397.3	1	5558.5	6
5125.9 3*	5 <b>3</b> 99·1	2	5563.7	4
5136.7 1	5403.3	4	5583.1	2
5140.4 2*	5404.3	2	5584.4	3
5148·9 1 * b	5406.3	1	5588.9	2
5161.6 1	5408.5	8d		
			,	

# DIFFERENCES.

a.	b.	C.	
36.0	$\frac{75.4}{2} = 37.7$	37.5	36.0
36.5	38.2	37.4	36.0
36.4	$\frac{76.6}{2} = 38.3$	38.3	35.1
$\frac{72 \cdot 2}{2} = 36 \cdot 1$	37.9	38.5	35.1
$\frac{73.4}{2} = 36.7$	39.0		35.4
35.9	38.7		35.0
	38.6		34.2
			35.3
			34.5

The series are not as pronounced in the case of the zinc excitation as in many of the other cases. Apparently the series which I have marked "a" and which is excited by the longest of the three zinc lines, appears to have its upper members excited by one of the other zinc lines, and not by the line which starts the series. In other words, the line 4883.6 seems to be the last line of the "a" series excited by Zn 4810.7, but we find a number of lines in the spectrum excited by the total radiation of the zinc lamp, which form a continuation of this series. Neither of the other zinc lines, however, falls at points determined by extending the series down to their region. We must remember, however, that when we stimulate the vapour in the blue region, the series which starts at the point of stimulation gradually dies out as we go up the spectrum, and other series make their appearance, a circumstance which explains the apparent difficulty just mentioned. There seems to be some evidence that as we ascend the spectrum the spacing between the lines of a series begins to grow less again, that is the spacing has a maximum value somewhere in the middle of the spectrum. Compare the series "a" and "d" for example. Too much importance must not be attached to these tables of differences, however, as the lines which belong together have been determined only from the older spectrograms, which are very unsatisfactory, and by spacing off the new spectrum chart with a pair of compasses. The resonance spectrum has now been photographed with the 12-foot concave grating, and as soon as the new zinc lamps arrive the spectra excited by the isolated zinc lines will be recorded with the same instrument.

#### Lithium Excitation.

The light of the lithium arc stimulates a most remarkable group of resonance spectra. It is the only means that I have yet found of exciting definite series of lines in the red region of the fluorescence spectrum. There are four exciting lines in all, but they are so widely separated that the resonance spectra excited by them only overlap to a very slight degree. A photograph taken on a panchromatic plate of the complete spectrum excited by the lithium arc is reproduced on Pl. XVIII. fig. 1. The points of excitation are indicated by arrows.

The blue line ( $\lambda=4603$ ) excites a resonance spectrum consisting of a nearly equidistant group of lines in the violet, and another group in the yellow-green. These two groups are indicated by the brackets "A."

The blue-green line ( $\lambda = 4972$ ) excites a remarkable series

of lines midway between the groups "A." This series is of especial interest, for, as will appear presently, the barium line 4934 takes hold of the same series, at the first line below the exciting line of the lithium series. The red and orange lines of lithium also excite two well-marked series in the red region of the spectrum, the individual lines of which appear to be very nearly equidistant. As yet I have not determined the wave-lengths of these lines, though they can be determined at any time from the plate which has an iron comparison spectrum running parallel to the resonance spectra. as a whole, this plate is the most beautiful illustration of resonance spectra excited by monochromatic stimulations, that I have obtained up to the present time. The photograph was made with a small two-prism spectrograph, and has not been used for wave-length determinations owing to the small dispersion and the great width of the slit. Spectrograms best suited to the accurate measurement of the lines do not reproduce very well, consequently I have used only those taken with a wide slit for purposes of illustration, and the possible accuracy of the wave-length determinations must not be judged from the photographs which accompany this paper.

We will now consider the series excited by the green-blue line 4972. The wave-lengths of the lines in this series are recorded in the following table. The wave-lengths I consider accurate to about three tenths of an Angström unit, as the plate was an especially good one, taken with a very fine slit.

	Di	fferences.
4862.0 *		20.0
4896.2*		39.9
4934.0 *		39·0 39·1
$4972 \cdot 3 *$		29.1
5007.4		39.2
5009.6		39 2
5011.7*		38.2
5049.9 *	•••••	30 <u>2</u>
5085.9		39.4
5089.1 *		
5117.8		38.3
5123.7	• * * * * * * * * * * * * * * * * * * *	90 9
5128.2 *		
51529		37.8
5162.4	***************************************	310
5167.2*		
5191.8	***************	34.2
5199.4	***************************************	01 Z
$5207 \cdot 1 * ?$		
5229.6 * *		37.3
5266.9 * *		37.4
53043 * *		014

In this table I have marked the lines which form the equidistant set with a star \*. The last three belong to a different series not continuous with the first. It will be seen that as we go up the spectrum other lines come in on the short wavelength side of the principal lines, as in the case of the series of doublets excited by the green cadmium line.

A discussion of the spectrum excited by the blue-violet lithium line will be postponed for the present, as I prefer to wait until photographs have been obtained with the large

concave grating.

### Barium Excitation.

The excitation by the strong barium line 4934 is of great interest as the same series is brought out as in the case of the lithium excitation. The point of excitation is at the first line below to the exciting line of lithium, and the resonance spectra are identical except that the companion lines which appear on the short wave-length side of the principal lines are not identical. The wave-lengths are given in the following table, the principal lines being marked with stars.

	D	ifferences
4896.2 *		37.8
4934.0 *		38.3
4972.3 *		90 9
5008.9		38.7
5011.0 *		
5046.6		38.7
5049.7 *		38.7
5088.4 *	••••••	90.1
5123.0		39.2
5127.6 *		
5130.8		
5160.9		39.5
5163.8		
5167.1 *		
5192.0		
5199.3		39.5
5202.3		
5206.6 *		
5238.0		
5240.0		
5299.5		
5327.7		
$5336 \cdot 2$		
5340.0		

The three strong lines of a different series, which appeared with the lithium excitation (double starred in the table), do not appear with the barium excitation.

### Thallium Excitation.

The great line of the thallium arc excites a resonance series of lines some of which are accompanied by companion lines on the short wave-length side. A photograph of the spectrum, taken with a wide slit, is reproduced on Pl. XIX. fig. 1. The wave-lengths are as follows:—

	D:	fferences.
5206 *	37).	nerences.
5235		36
5242 *		36
5278*	***************************************	-
5304 5314 *	••••••	36
5351 *		37
5387 *		36
5419		36.5
5423.5*		
5450	***************************************	36.5
5460 *		

The thallium arc burnt very steadily. The lower carbon, which was bored with a hole 2 mms. in diameter, was kept full of metallic thallium, and used as the anode.

The lines of the series are a little closer together in this case, as appears from the table of differences.

# Magnesium Excitation.

A great deal of time was wasted in trying to obtain a satisfactory magnesium are between metallic electrodes in hydrogen at low pressure. It was finally found that the simple expedient of introducing magnesium powder into a hollow carbon answered every purpose, the arc burning steadily. Fresh powder was put in every four or five minutes.

The green triplet (b group) excite brilliant resonance spectra, which are reproduced on Pl. XVIII. fig. 4. In this spectrum we find the triplet reproduced more or less perfectly at regular intervals. If the spacing of the individual lines forming the series was the same for each series, it is clear that we should have the triplet reproduced over and over again along the spectrum. That this is so only to an imperfect degree is due to the difference in the spacing of the lines of the different series. No means has as yet been found of exciting the spectra separately, owing to the proximity of the three exciting lines.

The wave-lengths are recorded below.

It is easy to pick out the three series of equidistant lines excited by the three magnesium lines, but it is impossible to tell anything about the extra lines or to which series any one of them belongs. Lines belonging to the same series are indicated by the same letter, while the exciting lines are underscored. The differences for the three series a, b, and c are given in a separate table. The series "a" is the best one obtained, so far as constancy of wave-length difference goes. The slight discrepancy at the middle of the table compensates itself, and is doubtless due to an error of half an Ångström unit in the determination of one of the lines.

5342 b	5145·5 b		DIFFERENCE	CES.
5327  a	5142.7		,	
5305	5140	a.	b.	c.
5302•5 b	5136 a	39	39.5	38.8
5297.2	5134.5	38	39	38.7
5296	5133	38	39.5	39
5288 a	5129 c	$38.5_{-}$	39.5	38.5
5286	5124	37.5	39	39.2
5284 c	5106.5 b	38	39	40
5263.5 b	5101	38	38.5	
5258	5098 a	38	38	
5250 a	5095.2	38	39	
5245·2 c	5089.8 c	38	-	
$5224 \ b$	5075			
5222	$5068 \ b$			
5212 a	5060 a			
5206.5 c	5056			
5201.5	5049.5 c			
5190	$5030 \ b$			
5184·5 b	5022 a			
	$4991 \ b$			
5181	4984 a			
5179	4978.5			
5173.5 a	4957			
5167.5 c	4946 a			
	-0-0			

#### Lead Excitation.

The lead arc causes the sodium vapour to emit a well-marked series of lines, with a wave-length difference of 39 Ångström units. These lines are accompanied by companion lines sometimes on one side and sometimes on both sides, as will be seen from the chart. The law governing the distribution of the companion lines and the possible cause of their appearance cannot be determined until a larger collection of photographs of the resonance spectra has been made and the results compared and tabulated.

The lines which form the series are marked with a star.

5336.5		
5309.5		
5299		
5272		
5263		
5254		
5238		
5233	Diff	ferences.
5201 *		
5195		90
5188	***************************************	39
5162 *		
5158		
5154	• • • • • • • • • • • • • • • • • • • •	39
5127		
5123 *		
5119.5		39
5084 *		
5081		39
5045 *		
5042	***************	<b>3</b> 9
5006 *		
5002	********	38
4968 *		
4963		38
4956	***************************************	90
4930 *		
4928		
4925		

The line in the lead spectrum which stimulates this resonance spectrum has a wave-length of 5006: there is in addition a weaker line at 5002, and I am not sure whether the light of this line is responsible for any of the spectrum. It comes within one Angström unit of fitting into the series, but it is much fainter than the 5006 line.

#### Bismuth Excitation.

The bismuth arc is by far the best exciter of the vapour which we have, and it furnishes the most typical resonance spectrum. It has but a single line which is operative, and this line is located in the remote blue. The resonance spectrum consists of a series in the blue, which with long exposures can be traced well up into the green, and a host of lines at the upper end of the spectrum in the yellow-green region.

The exciting line in the resonance spectrum is accompanied by two faint companions, one on each side, the first line above it is a close doublet, the second a wider one, and the first line below is a suspected doublet, judging by its width. In all probability the second and third lines below the exciting line are doublets, though they are so faint as to be only just discernible on the photographs obtained thus far.

The wave-lengths in the blue and green region are given in the following table. Two lines in the series appear to be missing.

5007 *	Differences	
5004 4995 4990 4962		36
4935 * 4927 4867		35.5
4864 * 4860 4828·5 *		35.5
4823.7 4793 * 4790.5		35·5 35·5
4757·5 * 4756·5 4727		34.5
4723 * 4720 4690 *		33 32·5
4657·5 * 4625 *		32.5

The lines in the yellow-green region are given below. The intensities are designated roughly by numerals, 1 meaning very faint.

5534.4	1	5447.1	$^2$	1	5391.9	
5530.3	1	5445.9	$^{2}$		5391.1	2
5509	1	5442.1	2		5388.3	1
5504	3	5440.9	5		5387.1	1
5500.9	6	5438.3	1		5379.1	4
5499.5	1	5436.7	1		5377.7	4
5491.6	2	5431.1			5376.2	1
5490.1	2	5429.5			5374.0	5
5488.7	5	5426.8		į	5373.5	7
5474.5	5	5425.4			5372.5	i
5473.5	6	5423.9		1	5358	2
5470.5	2	5413.2	8	İ	5357.3	2
5469.0	2	5411.9	8	i	5355.7	1
5463.8	1	5410.4	2		5336.8	6
5462.3	1	5408.3	5		5335.6	2
5459.4	7	5407.5	5	į.	$5334 \cdot 1$	1
5458.0	3	5394.8	2		5299.8	2
5456.5	5	5392.8				

# Silver Excitation.

In the earlier work it was believed that the silver line 5209 excited the same series as the cadmium line 4800. This is now known to be an error due to the insufficient *Phil. Mag. Ser. 6. Vol. 15. No. 89. May 1908.* 2 S

power of the spectroscope employed. The silver line excites a series, the individual lines of which are about 1.5 Angström units longer than the corresponding lines excited by the cadmium line. The silver arc employed in exciting the resonance spectrum was formed between carbons, the lower one of which was furnished with a core of metallic silver. No prismatic separation was required, as the line 5209 was found to be the only one capable of exciting the vapour. The wave-lengths of the lines in the resonance spectrum are given in the following table. The first six lines in the table were very faint, and their wave-lengths are not so accurate as is the case with the remainder.

	Dif	ferences.
4947.5		0 - 0
4985:3		37.8
5022:3		37
5059.5	*****************	37.2
0 0 0		37.5
5097-0		0.0
5122.0  a	****************	36
5133.0 *		
5160·0 a	***************************************	37.8
5170.8 *		
51980 a	***************************************	32.2
5209.0 *		-
5236 O a	***************************************	38
5247:0 *		
5285-0 *		38
5324.5 *		38.5
いりーエリキ		

The strong lines which have been measured with considerable accuracy, and which form a series, I have indicated with stars. The first five lines in the table also belong to the same series I think, though there seems to be a slight discrepancy in the table of differences. Four of the strong, equidistant lines are accompanied by faint lines on the short wave-length side. These four companion lines are also equidistant. They are marked "a" in the table, and their wave-length differences are exactly 38 A.E.

# Copper Excitation.

The resonance spectra excited by the light of the arc between electrodes of metallic copper are reproduced on Pl. XVIII. fig. 3. The three green lines are alone operative, and though the line 5293 appears on the plate I am of the opinion that no fluorescence is excited by it. Spectrograms have been obtained of the spectra excited by the three lines separately, but they are not very satisfactory, as the slits of the monochromatic illuminator had to be made very narrow and there was but little light available. To separate close

lines and still have enough light to work with is now the chief difficulty. I have recently found a chlorate of potash film which in transmitted light shows a very black interference band not much over 15 Ångström units in width. The position of this band varies with the angle of incidence of the light, and it can be set so as to cut off either one of the copper lines at will. It cannot, however, do this for a divergent beam of light, owing to the variation of the incidence angle in this case; and as the crystal is less than a square centimetre in area, little or nothing is gained by its use over the monochromatic illuminator. If we could prepare crystal flakes similar to this, measuring several cms. in width, they could be used with light made parallel by a lens, and the problem of separating spectrum lines would be solved.

In the resonance spectrum excited by the three green copper lines I have already measured over one hundred and twenty-five lines, but until more satisfactory spectrograms have been obtained with the separated radiations I prefer not to publish this table. The spectrum is very complicated, and I do not feel at all sure of the lines which belong together, although there are a number of very well marked series. My surmise of a year ago that the shortest of the three lines excited a series of doublets has been verified.

# The Magnetic Rotation Spectrum.

The present work has shown that there are not many coincidences between the bright lines of the magnetic rotation spectrum and the lines of the resonance spectra. The belief that these coincidences existed, which was expressed in the earlier paper, was due to the low dispersion used. There appear to be six or more series in the magnetic spectrum, but they do not coincide with any of the series excited by monochromatic radiations. The lines which show the magnetic rotation are the lines which come out with especial prominence in the spectrum of the fluorescence excited by white light. At the present time I am engaged in a study of the magnetic spectrum by the method described in my recent paper on the possible existence of positive electrons in the sodium atom.

I have photographed the spectrum over again under more favourable conditions, and have obtained a much larger number of lines, nearly 200 in all. The table of their wavelengths will not be published until the final paper is ready for publication, as I have not yet determined whether all of the lines rotate the plane of polarization in the same direction.

White Light and Cathode-ray Excitation.

At the close of the present year an attempt will be made to photograph the white-light fluorescence spectrum with the 21-foot grating in the second-order spectrum. This will give us a record on the same scale as the absorption-spectrum map. I have already found that the structure is much more complicated than was at first supposed, the darker regions between the strong lines being filled with a multitude of fine lines. The structure of the spectrum which I attempted to show with a drawing in one of the earlier papers is quite incorrect, the peculiar appearance being due to a peculiar distribution of the light in the spectrum, combined with a rather wide slit. The white-light fluorescence spectrum, which begins at about 4600, ends quite abruptly at the point where the yellow-green doublet of the first subordinate series

appears in the arc spectrum of the metal.

This may be an accident of course, but it may also be due to some relation between the parts of the vibrating mechanism, with which we are at present unfamiliar. The general appearance of the upper half of this spectrum is shown on Pl. XVIII. fig. 2 (upper spectrum), with an iron comparison spectrum. The upper end of this spectrum is also shown on Pl. XIX. fig. 3 (upper spectrum), together with the D lines which come out bright, and a portion of the red and orange fluorescence spectrum. The red-orange fluorescence extends a little below the D lines, but not quite down to the terminus of the vellow-green fluorescence, the region between the two spectra being destitute of light. The bands which border the edge of this black region give it the appearance of a deep chasm. I have already obtained some excellent photographs of this region, and they will be published with the final paper. Exciting the vapour with cathode rays causes it to emit a very remarkable spectrum. The lines of the principal and subordinate series come out with great intensity, as well as the lines which appear in the fluorescence excited by white In addition there is an entirely new spectrum, which in a way appears to be symmetrical about the D lines, at least in their immediate vicinity. This spectrum is shown on Pl. XIX. fig. 3 (lower spectrum). It is on the same scale as. and placed in coincidence with, the white-light fluorescence spectrum. The lines of the subordinate series I have marked with black dots. It is a very remarkable fact that the bright bands to the right and left of the D lines coincide with broad dark bands in the fluorescence spectrum. This scarcely shows on the print which I am reproducing, and it will in all probability disappear completely in the process of reproduction. I have some plates made a year ago which show the bands most beautifully, but I have not yet enlarged them,

and they are on too small a scale to reproduce well.

The present paper must not be regarded as a complete presentation of the subject, and I am publishing these results now in order that they may serve as a guide to those who are at work at the theory of the radiation of electron systems, from the theoretical side.

IVI. The Distribution in Electric Fields of the Active Deposits of Radium, Thorium, and Actinium. By SIDNEY RUSS, Demonstrator of Physics, Victoria University, Manchester\*.

#### Introduction.

THE distribution in an electric field of the excited activity produced by thorium and radium emanations has been studied by several observers. Working with thorium emanation. Rutherford + has shown that the amount of activity imparted to a rod charged negatively decreases as the pressure in the containing vessel is reduced after a certain pressure is reached; while experiments made by Makower t show that similar effects are obtained with the excited activity produced from radium emanation. Some further experiments by Rutherford & with the emanation from radium indicate that while at atmospheric pressure the greater part of the excited activity is directed to a cathode by moderate electric fields, yet a small fraction (about 5 per cent.) goes to an anode. Reasons are then (loc. cit.) given for supposing that some of the active deposit particles carry a negative charge, thus accounting for their transmission to the anode.

It seemed of interest then to find out whether the quantity of active deposit that goes to an anode changes when the

pressure is varied.

A comparison has therefore been made over a range of pressure extending from '001 cm. to 10 cms. between the amount of activity imparted to a rod charged positively and then negatively when exposed for the same interval of time to equal quantities of the radium emanation.

It was found that whereas the activity of the cathode decreased as the pressure was diminished, the anode showed

a corresponding increase in activity.

\* Communicated by the Physical Society: read March 13, 1908.

† Rutherford, Phil. Mag. Feb. 1900. † Makower, Phil. Mag. Nov. 1905. § Rutherford, Phil. Mag. Jan. 1903. The rod which had served as cathode or anode was then made a neutral pole by connecting it to the containing vessel, and what may be called diffusion experiments, *i. e.* with no electric field existing in the gas, were then made. Observatious showed that there was a marked decrease in the amount of active deposit that diffused on to the rod as the pressure was diminished.

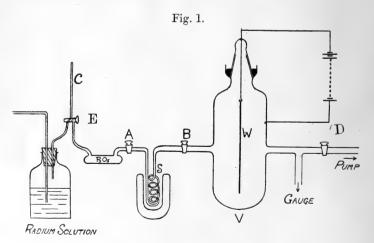
After a slight modification of the apparatus, a comparison of the activity obtained on a cathode and anode over a range of pressure extending from 1 mm. to 1 mm. was made with three gases having widely different densities, namely, hydrogen, air, and sulphur dioxide.

The results in the case of air show that the activity of the cathode is considerably greater than that of the anode, but that they approach equality as the lower pressure is reached.

This effect is more marked in sulphur dioxide, while for hydrogen no such difference in activity is observed, just as much active deposit being transmitted to the anode as to the cathode over this range of pressure.

# Methods of Experiment.

A comparison was first made between the amounts of excited activity obtained on a wire maintained at 200 volts acting as cathode and then as anode over a range of pressure extending from '01 mm. to 1.2 mm.



The apparatus used is represented in fig. 1. A brass wire W 10 cms. long, 55 mm. diameter, on which the active

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deposit was obtained, was suspended so as to hang symmetrically within the glass vessel V which was silvered on the inside, connexion to a battery of cells being made by means of a piece of platinum fused in the side of the vessel.

The usual method of experimenting was as follows:—

The whole system, with the exception of the vessel containing the radium emanation evolved from a solution of radium bromide, was exhausted firstly by means of a Fleuss pump and then by a charcoal tube immersed in liquid air (not shown in diagram). When the desired pressure had been obtained the tap D was closed, and by turning the tap E the small capillary tube C (·2 c.c. volume) was filled with the emanation at atmospheric pressure.

The tap B was then closed and the glass spiral S surrounded by liquid air, E was then turned and the emanation contained in the capillary C was allowed to pass over a tube containing  $P_2O_5$  for drying purposes, after which it condensed in the

spiral S.

A few trials showed that nearly all of the emanation had condensed in 15 minutes. The tap A was then closed, B opened, the liquid air removed from the spiral, and the emanation allowed to diffuse into the vessel V and a McLeod gauge which was in connexion with it. The resulting pressure was then read.

As the volume of the  $P_2O_5$  tube was several times that of the spiral, quite low pressures were obtainable in the spiral although the capillary C had been filled at atmospheric pressures. The wire W was made either a cathode or anode as desired and exposed to the emanation for 1 hour. It was then removed from the vessel V, and its activity tested in the usual way by making it the central electrode of a cylinder connected with a Dolezalek electrometer and measuring the ionization produced by the  $\alpha$  rays emitted from it. The electrometer leak obtained in a measured interval of time 14 minutes after the removal of the wire from the emanation was taken as a measure of the activity obtained on the wire.

The variation in activity with change of pressure is seen from Table I., also from fig. 2, where the abscissæ represent pressures and the ordinates the corresponding activities of the wire. It will be seen from the diagram that there is a very large decrease in the activity of the cathode as the pressure is diminished, while the anode shows if anything a small increase; the amount obtained by diffusion alone, i. e. to a neutral rod, being practically constant over this range of pressure.

It will be observed that whereas at a pressure of about

TABLE 1.

Positive Electrode.		NEGATIVE E	NEGATIVE ELECTRODE.	
Pressure in mms.	Activity.	Pressure in mms.	Activity	
.011	69	•006	142	
·013	79	.008	189	
·137	84	•102	173	
191		·125	157	
202	81	476	425	
250	62	.729	736	
.608	63	1.165	1118	
792	67	NEUTRAL ELECTRODE.		
		Pressure in mms.	Activity	
.865	56	152	72	
922	56	435	64	
1.102	57	•722	57	
		1.140	62	

1 mm. the activity of the cathode is about 20 times that of the anode, at '01 mm. it is only about twice as much.

At this stage of the work it was decided to compare the activities of the cathode and anode at much higher pressures.

Several trials with the apparatus just described were made at pressures higher than 1 cm., but discordant results were obtained. This was probably due to the emanation being blown back into the spiral on allowing air to enter the vessel V, which was initially well exhausted as in the previous

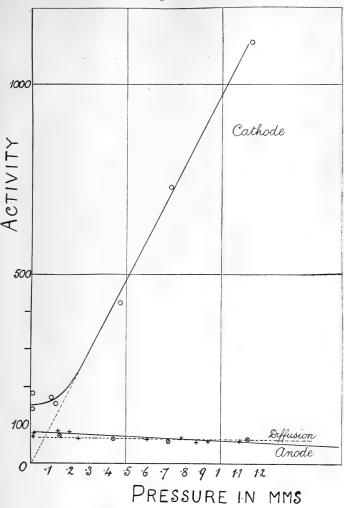
experiments.

For this reason observations were made with a modified system consisting simply of a brass cylinder down the centre of which passed a brass rod (provided with end-pieces to ensure uniformity of field) which was connected to cells giving the same voltage as before. The brass cylinder was connected on one side with a small vessel which was filled with the emanation at atmospheric pressure, and on the other with a pump and pressure-gauge.

The small vessel containing the emanation was provided with metal electrodes, and the precaution was taken of applying a strong electric field to the emanation before letting it into the brass vessel; this removed any active deposit or

dust particles.

Fig. 2.



The system was initially exhausted to about 1 mm. pressure, the emanation then let in and the small vessel isolated from the cylinder, the pressure in which was then adjusted to whatever value was required. The activity obtained on the brass rod after one hour's exposure was measured in exactly the same way as before. Observations were made for a range of pressure extending from 2 mms. to 10 cms. The numerical data are contained in Table II., and the results shown

graphically in fig. 3, where abscissæ denote pressures and ordinates the corresponding activities.

TABLE II.

Positive Electrode.		NEGATIVE ELECTRODE.	
Pressure in cms.	Activity.	Pressure in cms.	Activity,
.13	152	·13	780
·27	140	2:04	1360
.55	163	2.70	1400
50	109	7.22	1540
.63	148	7.80	1470
1.10	120	NEUTRAL ELECTRODE.	
3.78	94	Pressure in cms.	Activity.
6.24	79	•36	219
7:30	77	•40	198
		3.14	287
8.94	77	3.74	300
10.96	75	8.44	447
		8.82	437

It will be seen that whereas the activity of the cathode decreases with diminishing pressure, there is a very marked increase in the activity of the anode, while the amount of active deposit that diffuses on to the neutral rod decreases very considerably as the pressure is reduced.

Diffusion experiments similar to those just cited are at present being made, in which, however, other metals than

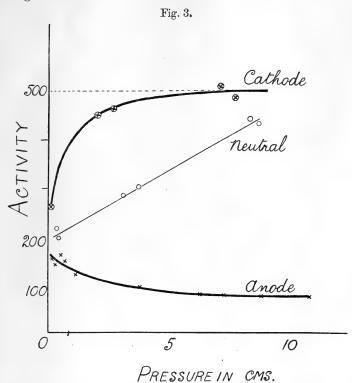
brass are used as containing-cylinder and rod.

It will be seen from fig. 3 that at a pressure of about 2 mms. the quantity of active deposit transmitted to the anode is approximately equal to that diffusing on to a neutral

pole.

Now the active deposit that diffuses on to a neutral pole we have seen to be in the main positively charged (the bulk of it going to a cathode in an electric field). Very little of this positively charged matter can make its way to the anode. In order to account for the quantity obtained on the anode we are led to the conclusion that some at least of the active deposit particles that make their way to the anode are negatively charged.

The above results then go to confirm the view held by Rutherford already referred to, that the active deposit particles which are directed to the anode have a negative charge.



The activity of the cathode being much larger than the anode, the scale in fig. 3 for the cathode is one third that for the anode and neutral pole.

It has been suggested by Rutherford\*, in explanation of his results with thorium emanation, that the decrease in activity of the cathode as the pressure is reduced is due to a decreasing number of collisions between the active deposit particles and the gaseous molecules with which they are mixed.

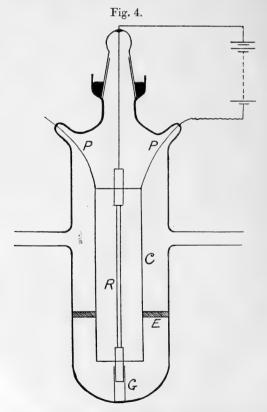
At the moment of expulsion of an  $\alpha$  particle from the emanation atom, the residue, *i. e.* the active deposit particle, acquires a velocity in the opposite direction, which, though

<sup>\* &#</sup>x27;Radioactivity,' p. 319.

small compared with that of the  $\alpha$  particle, is high compared with the velocity of an ordinary gaseous molecule.

On the view above cited a certain number of collisions with the gas molecules is necessary to sufficiently reduce the velocity of the active deposit particles in order that moderate electric fields may direct them to cathode or anode.

Hence we might expect the effectiveness of a molecular encounter to depend on the nature of the gaseous molecules with which the active matter is associated. Experiments to test this point were therefore made with three gases differing considerably in molecular constitution, namely, air, hydrogen, and sulphur dioxide, and a comparison between the activities of cathode and anode over a range of pressure extending from '1 mm. to 1 mm. was made with the low pressure system already described. The silvered vessel was,



however, replaced by another glass vessel containing two concentric cylinders as seen in fig. 4.

The inner one R, 7 cms. long and '36 cm. diameter, acted as the rod upon which the active deposit was obtained, C the outside cylinder, 8'95 cms. long and 2'7 cms. diameter, being suspended by two platinum wires PP which were sealed into the glass vessel and connected to either pole of the battery as required. The ebonite ring E kept the outer cylinder steady, and the rod R was supplied with a guard-ring at each end, one of which fitted into a glass tube G, thus serving to keep the rod central within the cylinder C.

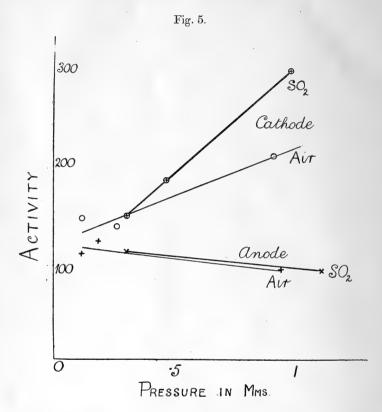
These modifications were adopted so as to ensure a uniform electric field between the rod and cylinder, and also to render the problem more accessible to mathematical treatment, the areas of the rod and cylinder being not very different. With this arrangement experiments with the gases already mentioned were made, and the results obtained are collected in Table III. and reproduced graphically in figs. 5 and 6.

TABLE III.

Air.		Sulphur Dioxide.		
Pressure in mms.	Activity.	Sign of Electrode.	Pressure in mms.	Activity.
·115	108	Positive.	·302	111
185	122	,,	1.120	93
.931	95	,,		
·115	146	Negative.	297	148
.260	137	27	.462	184
•902	211 -	,,	.970	298
	Pressure in mms.  115 185 931 115 260	Pressure in mms. Activity.  115 108 122 931 95 115 146 260 137	Pressure in mms.         Activity.         Sign of Electrode.           •115         108         Positive.           •185         122         "           •931         95         "           •115         146         Negative.           •260         137         "           •902         211         "	Pressure in mms.         Activity.         Sign of Electrode.         Pressure in mms.           ·115         108         Positive.         :302           ·185         122         ,,         1·120           ·931         95         ,,            ·115         146         Negative.         ·297           ·260         137         ,,         ·462           ·902         211

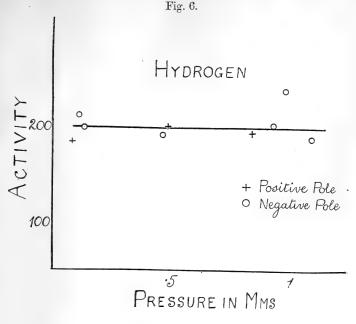
	Hydrogen.	
Sign of Electrode.	Pressure in mms.	Activity.
Positive.	.084	184
2.7	•481	200
29	·828	194
Negative.	·116	212
"	·131	198
,,	.462	192
"	925	202
9.9	•970	239
"	1.080	188

It will be seen that for SO<sub>2</sub> there is a much greater difference in the activities of cathode and anode than is the case for air, while for hydrogen practically no difference in activity over the same range of pressure was obtained.



We should expect that the curves for cathode and anode in the case of hydrogen would show a divergence at higher pressures, for if an encounter between the active deposit particle and a hydrogen molecule is not so effective in reducing the velocity of the former as a sulphur dioxide molecule, then we shall require a higher pressure with hydrogen to observe the same effects as with sulphur dioxide.

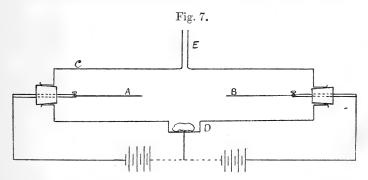




### Thorium and Actinium.

A few experiments made with the emanations from thorium and actinium show a rather striking difference in the distribution of their active deposits in an electric field.

The experimental arrangement seen in fig. 7 was used.



Two thin brass wires 7.5 cms. long and .7 mm. diameter were made to lie along the axis of a brass tube C 30 cms. long and 4.2 cms. diameter. This tube was fitted with a small capsule D, into which was placed a small quantity of

thorium oxide, or of a preparation of actinium kindly lent me by Professor Rutherford.

The wire A was connected to the positive, B to the negative pole of a battery giving 320 volts, the brass tube being connected to the middle point.

The exit-tube E was connected to a Fleuss pump and a set of tubes containing calcium chloride and cotton-wool, thus ensuring a supply of dry and dust-free air.

When experimenting with thorium the wires were exposed to the emanation for 24 hours, after which they were removed and their activities tested with an electrometer in the manner already described.

The ratio of the activities of the cathode and anode at atmospheric pressure was found to be about 200:1; on reducing the pressure to 2 mms. the ratio was diminished to 25:1, this reduction being mainly due to the decrease in activity of the cathode already observed by Rutherford (loc. cit.). No certain increase in the very small activity of the anode was observed.

In the experiments with actinium the wires were exposed usually for about 2 hours.

At atmospheric pressures the ratio of the activities of the cathode and anode was about 2 to 1, while at 2 mm. pressure it was 22 to 1, the *increase* in the ratio being mostly due to an increase in the activity of the cathode. The active deposit on the two wires decayed at the same rate, namely, that of actinium A.

These results show that while the greater part of the active deposit from actinium emanation has a positive charge, yet at amospheric pressure a very considerable fraction has a negative charge, and is therefore directed to the anode.

For purposes of comparison the activities obtained on a wire when exposed to the emanations of Ra, Th, and Ac at atmospheric pressure are tabulated.

		Wire charged negatively.	Wire charged positively.
Thorium		200	1
D 1.		200	10
Actinium	,	200	100

### Conclusion.

In view of the different distributions in an electric field of the active deposits of thorium, radium, and actinium, it is difficult to think of the whole series of events between the formation of the active deposit and its transference to either electrode, as taking place in an exactly similar fashion.

It has been shown by Miss Slater\* that slowly moving  $\beta$  particles accompany the  $\alpha$  particles which are ejected from thorium and radium emanations. If there are two such  $\beta$  particles to every  $\alpha$  particle, the remainder of the emanation atom, *i. e.* the active deposit, would be left with a positive charge.

This supposition would explain the almost complete transference of the active deposit of thorium to the cathode; but the small, though quite definite, quantity of the active deposit of radium that is directed to the anode still presents

deposit of radium that is directed to the anode still presents a difficulty. It may be that a few of the active deposit particles *gain* negative ions from the gas in which they are moving, which must be present in very large numbers.

In the case of actinium, although at a pressure of a few millims, far more activity is observed on the cathode than on the anode, as has already been found by Debierne†, yet we have seen that at higher pressures this inequality is very much reduced, there being almost as many negative carriers as positive.

It is hoped that a more extended series of observations may throw some light on the apparently anomalous behaviour of actinium.

In conclusion, I desire to thank Professor Rutherford for several suggestions during the latter part of the work. The research was begun with Mr. Makower, who, however, could not continue the collaboration owing to pressure of other work. I wish to express my thanks for the very considerable help he has given me in these experiments.

#### Note added March 17th.

Some recent experiments made with actinium tend to explain the anomalous behaviour referred to above. A preparation of actinium was placed at the bottom of a cylinder, and two parallel plates were suspended so as to hang vertically above it. These plates were connected to the terminals of a battery of 300 volts, and after an exposure at atmospheric pressure usually lasting several hours the activities of the two plates were compared by means of an electroscope. The distance of the plates from the actinium preparation could be altered as required.

<sup>\*</sup> Phil. Mag. Oct. 1905.

<sup>†</sup> Comptes Rendus, vol. exxxvi. p. 671.

As already observed in the experiments described, the activity of the cathode was always greater than that of the anode.

It was found that when the plates were fixed at a distance of 4 cms. from the actinium, the ratio of the activity of the cathode to that of the anode was about 5 to 1; on bringing the plates nearer to the actinium this ratio rapidly increased, and when the distance was reduced to 2 mms, the activity of the cathode was more than a hundred times that of the anode.

These observations and others of a similar nature at different pressures (details of which it is hoped will appear in a future number), indicate that the sign of the electrical charge exhibited by the active deposit particles is some function of the distance which they have travelled through the containing gas, before reaching the electrodes.

LVII. The Electrochemical Equivalents of Oxygen and Hydrogen. By R. A. LEHFELDT, D.Sc., Professor of Physics at the Transvaal University College \*.

THE present investigation is an attempt (a) to design a gas-coulometer (voltameter) suitable for exact measurement; (b) to find how far the electrolysis of various solutions gives the calculated yield of gas; (c) to use the instrument to determine the electrochemical equivalents of oxygen and hydrogen.

In its general design the coulometer follows the accepted

methods of gas-analysis.

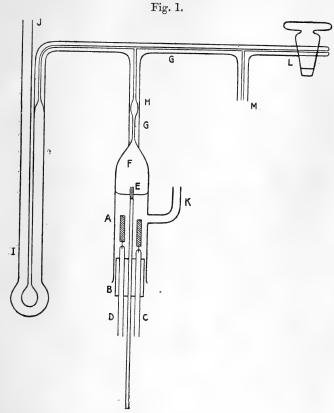
# DESCRIPTION OF APPARATUS.

The coulometer itself is shown in fig. 1. It is made entirely of glass. The tube A, in which the electrolysis takes place, is about 22 mm. diam. and 70 long. It is closed below by a rubber stopper B carrying the electrodes C and D and the inverted thermometer E. The electrodes are of platinum, usually about 3 sq. cms. each, welded to platinum wires which are sealed through the glass tubes. The tubes are about half a millimetre in internal diameter, with an enlargement at the top where the platinum wire is sealed through; they can consequently hold mercury even when inverted, and current can be led in and out by means of copper wires (No. 30 gauge) pushed up from below.

The thermometer E is required for the temperature of the

<sup>\*</sup> Communicated by the Author.

waste space F at the top of the wide tube, as the electrolyte rises in temperature considerably during passage of the current.



The connecting tubes G G are about 1 mm. in bore, but there is an enlargement H to catch drops of electrolyte projected upwards by the current of gas. K is a side tube for introducing the electrolyte, and is closed by a rubber tube and glass stopper.

is at the pressure of the atmosphere. Mercury, water, and olive oil were tried in this gauge, and the last found to be much the best. The gauge-tube is about 6 mm. in bore, and no error due to capillary action could ever be detected when oil was used. The gauge should be rather long, as when the gas to be measured is left for some time in the apparatus there is a risk of oil being sucked into the coulometer, in

consequence of changes of temperature. The gauge-tube should, for convenience, have either a rubber tube and stopper, or a tap to close it at the top when necessary.

The tap L allows of communication with the atmosphere. The descending tube M is connected by a rubber joint with

the gas-burette or measure-tube.

The coulometer was, of course, thoroughly tested for

leakage.

The measure-tube was about 35 mm. in diameter, and contained 200 c.c. It was drawn out at the top to connect with M, and at the bottom to lead to a three-way tap. One side of the tap leads to a mercury reservoir, from which the mercury in the measure-tube is supplied before an experiment; the other side of the tap allows the mercury, as it is displaced by gas, to flow out into a bottle.

The measure-tube is surrounded by a glass water-jacket like a Liebig condenser, through which tap-water flows continuously; and the temperature is taken by a thermometer

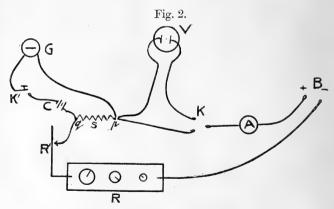
inserted at the top of the jacket.

At first a graduated tube was used, but this was given up in favour of weighing the displaced mercury each time.

The coulometer and measure-tube are supported by a

retort-stand.

The electrical connexions are shown in fig. 2. Current is



taken from a battery of ten accumulators, each of about 60 ampere-hours capacity. It is led through an ammeter A, to the three-part plug-key K by means of which the coulometer V may be cut out of circuit if desired. During the actual experiments the current flows through the coulometer to one terminal of S, the standard resistance, and from the other terminal to the rheostats R, R'. Of these, R is a dial

resistance-box giving tens, units, and tenths, and capable of standing the current used (0.6 ampere at the most). R is a fine adjustment, which though very simple is, so far as my experience goes, new, and proved extremely satisfactory. It consists of a glass tube (1 mm. bore, 25 cms. long) closed at the bottom; a platinum wire is sealed through the bottom, the tube filled with mercury, and a steel wire inserted at the top. By pushing the wire down or pulling it up, the resistance of the circuit can be adjusted with ease and certainty to a thousandth of an ohm.

By adjusting R and R', the potential difference between p and q is kept constantly equal to one, two, or three cadmium cells C by means of the galvanometer G. The cells, which were made in the laboratory, are kept in a

water-bath.

G is a direct-reading galvanometer, by R. Paul of London, indicating nearly one scale-division per microampere.

K' is an ordinary tapping key, kept down when desired by

a weight.

### CONDUCT OF AN EXPERIMENT.

The electrolyte having been filled in, current is started, with the tap L open. The current is then adjusted so that the cadmium cells are balanced, and is left flowing for a few minutes. The coulometer is usually covered with a wet rag to keep its temperature down. When the current is steady, all the temperatures are noted. Current is broken for fifteen seconds, during which time the tap L is closed, and a readjustment of the rheostat is made: this is necessary because the gas-bubbles in the coulometer increase its resistance; hence, after the break of fifteen seconds the current would be stronger than before and out of balance. With practice, the rheostat can be adjusted so that the current is almost exactly balanced immediately the circuit is remade. The plug of key K is then inserted at a precise moment by the chronometer, and attention devoted instantly to adjusting the rheostats, while an assistant turns the tap of the measuretube to allow the mercury to flow out at such a rate as to keep the gauge I level. After the first minute one observer can attend to both matters, and it is easy to keep the mercury flowing so that the pressure of the gas in the measure-tube is never more than a centimetre or two of oil above or below the atmospheric pressure. Under favourable circumstances the electric current can be kept steady as exactly as the galvanometer can be read, which is about  $\frac{1}{30,000}$  part; and of course, even when there are sensible fluctuations, they are sometimes

on the side of too much current, sometimes too little. The galvanometer-key is kept down by a weight throughout.

Shortly before the close of the necessary period the galvanometer-key is raised, tap of the measure-tube closed, so as to leave a slight excess pressure in the apparatus; the current is then stopped, and all temperatures taken again. The apparatus is left for a few minutes till the coulometer has regained its initial temperature, to within a degree or so; mercury is then run out till the oil-gauge is level, the temperature of the water-jacket taken, the barometer read, and the mercury weighed.

## DISCUSSION OF ACCURACY ATTAINABLE.

#### 1. Electromotive Force.

The cadmium cells used as a standard were made in the laboratory; the set of four on which most dependence was placed being of date August 1907. Of these, three were made with mercurous sulphate prepared electrolytically by Carhart's method; the other with sulphate bought from Merck: there was no appreciable difference between the two makes, however. The cells were all made with cathodes of mercury deposited electrolytically on platinum, and in the usual H form. They were kept side by side in a metal waterbath, with a thermometer. Comparison of the cells, made from time to time, showed hardly any systematic differences. Such differences as were noted, averaging three or four hundredths of a millivolt, appeared to be due to temperature variations—despite the water-bath: this would hardly be the case in most laboratories, but the extreme temperature fluctuations in a temporary corrugated-iron building in such a climate as Johannesburg, constituted the greatest difficulty in the way of accurate measurement; the temperature would sometimes vary from 8° to 22° C. in the course of the morning. The discrepancies between the cells do not really matter, however, as no combination of them would differ by so much as  $\frac{1}{20000}$  from another. As to the absolute values, though the cells have not been compared with any in Europe, experience elsewhere seems to show that the cadmium standard is quite reproducible to one part in ten

The value used is that given in a private communication from Mr. F. E. Smith, of the National Physical Laboratory, and based on experiments with the ampere balance:—

 $E_t = 1.01830 - 0.000034_5(t-17) - 0.00000066(t-17)^2$ .

# 2. Resistance.

The working standards were a pair of ten-ohm coils by R. Paul, used either singly or in parallel. These are made of "eureka" (constantan), and tested between 0° and 25° seemed to have no temperature-coefficient exceeding one or two millionths. The coils are enclosed in brass cases, with terminals at the top. This is not the best pattern of standard coil; but the errors involved in the way of terminals and connecting straps would not exceed one or two ten-thousandths of an ohm at the most, and are therefore quite negligible.

The largest current used through either coil was 0.3 ampere, the power spent being 0.9 watt. The heating due to this would not cause any thermoelectric error, as the coils are quite symmetrical; but it seemed possible that, with a combination of such large thermoelectric power as eureka and brass, the Peltier effect might introduce an error. This is so in theory, for the current entering at p would heat that junction and cool q. Hence a thermoelectromotive force will be set up, acting against the current, and the potential difference between p and q will be increased.

A special experiment was made to test this, by means of a potentiometer; but nothing measurable was found. As an additional precaution, however, the brass case was filled w

paraffin oil.

The absolute values of the resistances were obtained in the following way:—The laboratory possesses two platinum-silver standards, of 1<sup>ω</sup> and 100<sup>ω</sup> respectively, made by Nalder Bros., and tested at the National Physical Laboratory. The values are stated to be

 $0.99978^{\omega}$  at  $17^{\circ}.00$ . 2170 N. Ph. L.  $99.925^{\omega}$  at  $17^{\circ}.00$ . 2171 N. Ph. L.

There were also two eureka coils of 1° and 100° similar to the working standards. The eureka 1° and 100° were compared with the platinum-silver standards by a Lehfeldt comparator. In this comparison the same thermometer was used as for the gas-measurement (vide infra), and the temperature was within a degree of 17°. (It should be mentioned that this measurement was made in a well-built private house, where the temperature fluctuations were much smaller than in the laboratory.) The temperature coefficient of the platinum-silver was assumed to be 0.000247.

The two ten-ohm working standards were compared with each other similarly, and then combined with the 1<sup>ω</sup> and 100<sup>ω</sup> to make up a Wheatstone bridge, the 1<sup>ω</sup> being shunted

till balance was obtained. In this way two equations were arrived at giving  $(10 \text{ A}) \times (10 \text{ B})$  and  $(10 \text{ A}) \div (10 \text{ B})$ .

The final results were

$$(10 \text{ A}) = 9.9986$$
  
 $(10 \text{ B}) = 9.9981$ ,

in terms of the ohm as determined at the National Physical Laboratory, and it is hardly possible that the error can exceed  $\frac{1}{20.000}$ .

## 3. Time.

This was determined by a chronometer (Carroll, London, No. 505) beating half-seconds. Its rate was not studied with care, but was only two or three seconds a day-a negligible amount. The duration of the experiments varied from 1350 sec. to 4050 sec. There seemed in this the possibility of a serious error in timing the make and break of circuit by a plug-key, so special experiments were made to test it—with somewhat surprising results. The current being adjusted beforehand as usual, electrolysis was carried on for a period of five or ten seconds, and the mercury weighed in the ordinary manner. This gives a value for the quantity of electricity flowing that would be affected by the error of starting and stopping, and also by the error in the initial adjustment of current already spoken of. following short table shows that the two errors combined amount to much less than a tenth of a coulomb, i. e., much less than  $\frac{1}{10,000}$  in the main experiments.

Time.	Current.	Quantity of Electricity.  Calculated. Observed.		
seconds.	amperes. 0·509	coulombs.	coulombs.	
7	0.509	3.56	3.53	
5	0.509	2.55	2.54	
10	0.509	5.09	5.12	

A further possibility of error lies in the adjustment of the current; but, as remarked above, the galvanometer allowed of detecting a want of balance amounting to  $\frac{1}{30,000}$ , and as during a long experiment the current was sometimes

too large and sometimes too small, this possibility may be disregarded. Altogether, reviewing the electrical measurements—E.M.F., resistance, time, and current balance, one seems justified in considering that the quantity of electricity flowing is known to within one ten-thousandth part.

#### 4. Volume.

The mercury displaced by the gas was weighed on a large Oertling balance, capable of carrying five kilos and sensitive The weighing was only carried out to a to a milligram. decigram, however, as this is ample for the purpose, some 2500 grams of mercury being used in an experiment. The arms of the balance were found to be sensibly equal: the weights consisted of a 2000 g. and 500 g. in brass from a rough set, and 200 g. downwards from an ordinary box of analytical weights; the relative errors—amounting to 2 or 3 decigrams, in the case of the largest—were allowed for, the analytical weights being taken as standard. The relative accuracy of the weighing may be put at  $\frac{1}{50,000}$  therefore: but as to the absolute values I am unable to speak, there being no standard in this country. It is, however, hardly likely that the errors of the 200 g. and 100 g. in a box of weights of first quality would be large enough to matter.

The volume of the mercury was calculated from the table in Landolt & Börnstein, p. 42: temperature taken being the mean between the initial and final temperatures of the water-jacket. In favourable cases this only varied one or two tenths of a degree during the experiment, so that the error in the density of mercury would be of the order of  $\frac{1}{60,000}$ . The accuracy with which the amount of mercury flowing out could be adjusted was less than this, a single drop making a difference of one, ten, or twenty thousandth;

but it was sufficient.

#### 5. Pressure.

The barometer used was one of special design made for the author by Messrs. Baird & Tatlock, and filled in the laboratory. The tubes, of 25 mm. bore, are large enough to eliminate capillary effects; the upper tube carries a glass pointer to which the mercury was adjusted \* by means of an inlet and outlet tap, and a screw-clip compressing a short piece of rubber tubing. The mercury used was taken direct from the bottle in which it was supplied, and cleaned with

<sup>\*</sup> The barometer varies very little all the year round at Johannesburg.

nitric acid. The filling was done from the top by a Töpler pump, and the vacuum tested by the discharge between a

pair of electrodes in a side tube.

The height is measured by a pair of glass scales by Zeiss, each 20 cm. long, mounted on a strip of plate-glass which forms the back of the instrument. This arrangement was sent by the manufacturers to the National Physical Laboratory to have the distance between the short scales measured. To read the barometer the level at the top was adjusted to touch the glass pointer, and that at the bottom read by a telescope with micrometer eyepiece divided in hundredths of a millimetre. The mercury surface was illuminated from behind, through a little tissue-paper window into an adjoining room, where an incandescent lamp was placed. The level of the pointer was found to be 87.84 mm. on the upper scale; the distance between the zeros of the two scales 600.09 mm. at 15°2, according to the certificate of the National Physical Laboratory. Hence the uncorrected reading at 15° is the reading of the mercury against the lower scale (s) + 600.09-87.84.

From this must be subtracted the expansion of the mercury between 0° and 15° (on an average height of 622 mm.),

$$15 \times 622 \times 0.0001819 = 1.70 \text{ mm.}$$

and for gravity, according to the provisional value obtained (Lehfeldt, Phil. Mag., Nov. 1906),

$$\frac{978 \cdot 7 \sim 980 \cdot 62}{980 \cdot 62} \times 622 = 1.22 \text{ mm}.$$

The constant of the barometer is therefore

$$600.09 - 87.84 - 1.70 - 1.22 = 509.33$$
 at 15°.

The temperature coefficient is

$$(0.0001819 - 0.0000087)622 = 0.108 \text{ mm./degree.}$$

Hence the pressure of the atmosphere is

$$s + 509.33 - 0.108(t - 15),$$

where t is the temperature of the barometer.

The pressure of the gas-burette could usually be adjusted to differ from that of the atmosphere by not more than about

 $\frac{1}{4}$  mm. of oil (=1/60 mm. mercury).

The gas-burette was kept constantly moist by a few drops of water over the mercury, and the vapour-pressure of water at the temperature of the final adjustment was deducted from the observed pressure.

## 6. Temperature.

The most important temperature to record was that of the water-jacket of the gas-burette. This was taken by a thermometer (graduated in ½ degree) near the exit of the water. This thermometer had been compared with a standard that had been tested at the Reichsanstalt, and showed, over the atmospheric range of temperature, only irregular variations amounting to about 0°·06 as a maximum. The standard itself was tested at the freezing and boiling points and found to be exact, as stated in its certificate.

The water-jacket sometimes rose and sometimes fell in temperature during an experiment: in unfavourable cases as much as 1.5 degrees; sometimes only one or two tenths of a degree. The final reading, taken immediately after the outflow of mercury had been adjusted, might sometimes be uncertain to the extent of  $0^{\circ}.04$  or  $0^{\circ}.05$ : this is probably the most serious error in the experiments; it affects the reduction of the gas both directly and through the vapour-pressure of water, so that an error of  $0^{\circ}.05$  means about  $\frac{1}{3000}$  to  $\frac{1}{4000}$  on the result.

The other temperatures noted were:—

(a) Barometer: owing to the rapid fluctuations in room-temperature, the mercury of the barometer may at times have been a degree or more different from the attached thermometer. This would affect the pressure by  $\frac{1}{6000}$ .

(b) Cadmium cells: the influence of this is very small, and has been allowed for above.

(c) Air.

(d) Coulometer: a correction has to be made if the temperature of the coulometer is not the same at the beginning and end of the experiment. The coulometer itself was calibrated for volume, so that the amount of gas in it could be determined. If this was say 2 c.c., and the burette held 190 c.c., one degree makes a difference of

$$\frac{1}{290} \times \frac{2}{190} = \frac{1}{28,000}$$

in the volume of gas.

The temperature of the coulometer was allowed to fall after the experiment to nearly the same level as before, and the mercury then adjusted: the above correction was consequently always small.

The uncertainties introduced by fluctuations of temperatures are certainly the most important, and show that the results given below are about on the limit of the accuracy

obtainable by this apparatus.

### RESULTS.

## (a) Coulometer for exact measurement.

The electrolysing cell and gas-burette as described are suitable for measuring quantities of electricity up to 800 or 1000 coulombs; all the measurements can be made within ten minutes or so of the stoppage of the current, and the quantity determined to within one-tenth per cent. Further, the apparatus can be got ready for use again by the manipulation of a few taps, instead of the tedious chemical processes required by the silver voltameter.

If the gas be measured against that in a compensating bulb, as described by Hempel ('Gas-analysis'), the measurement is still more easy and rapid, though probably with a

slight loss of accuracy.

## (b) Electrolysis of various Solutions.

. The quantity of gas given off was measured in the cases of:—

	Strength. Per cent.	Per cent. of theoretic yield.
$H_2SO_4\dots$	10	99
NaOH	10 to 25	98·5 to 99·8
Na <sub>2</sub> SO <sub>4</sub>	10 to 30	Exact.
$Na_{2}S_{2}O_{3}$	10	53 (deposited sulphur).
Na HPO	10	97.5 to 99.7
Na <sub>2</sub> CrO <sub>4</sub> · · · · ·	10	99.5
KI	20	62 (turned brown, and
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	5 to 10	Exact. frothed).
$Na_{2}C_{2}O_{4}$	Saturated	91 (frothed).
Na HAsO	10	97
NaÑO <sub>3</sub>	10	50
NaClO <sub>3</sub>	10	33
•		

It appears, therefore, that sodium sulphate and potassium bichromate are the best electrolytes to use in the coulometer; no systematic differences could be detected between them, or between solutions of different strengths, or at different temperatures. There is, then, every reason to suppose that the electrolysis of these solutions is quantitatively correct.

Sodium hydroxide, contrary to what is usually stated, does

# not seem to yield better results than sulphuric acid.

# (c) Electrochemical equivalent of Oxygen and Hydrogen: value of the "Faraday."

One "faraday" of electricity (the amount associated with one gram-equivalent of matter) decomposes 9.0075 grams of water, yielding 8 grams of oxygen and 1.0075 of hydrogen.

If these be collected mixed under N.T.P. they occupy a volume

$$\frac{8}{0.0014290} + \frac{1.0075}{0.00008986} = 16809.9 \text{ c.c.},$$

using the best published values for the density of oxygen and hydrogen.

But as the water has a volume of 9 c.c., the increase in

volume is 16800.9 c.c.

The experiments with sodium sulphate and potassium bichromate detailed in the appendix—all the experiments to which no exception could be taken on account of the electrolyte, or for other reasons, give the following values for the gas evolved per coulomb:—

0.17396	0.17390	0.17398	0.17401
398	391	394	. 398
389	387	401	388
391	388	396	404

The mean is 0.17394, with a probable error of  $\pm 0.00001$ . Hence the value of the faraday

$$16800.9 \div 0.17394 = 96590$$
 coulombs.

The corresponding value for the electrochemical equivalent of silver is

$$\frac{107.93}{96590} = 0.0011174$$
 gram per coulomb.

This is lower than the value legally adopted (0.001118) on the basis of Kohlrausch and Rayleigh's experiments, but in close agreement with the latest work of Richards.

P.S.—An attempt was made to allow for the deviations from the laws of gases. But the deviations for oxygen and hydrogen being of opposite sign, the total effect is too small to be worth taking into account. The uncertainty in the density of the gases is larger.

The experiments were carried out in the temporary physical laboratory of the Transvaal University College; and some trials have been made there with a double apparatus, which, it is hoped, will avoid some of the sources of error. As, further, a well-constructed permanent laboratory is in course of erection, it may be possible to get still more concordant results. The author wishes to express his indebtedness to Miss Winifred Judson, B.Sc., for much assistance in the work.

December 1907.

APPENDIX.—TABLE I.

77. 78.	R. A. L. R. A. L.	.07. 12h. 13·8·07. 15h.	/o- do.	$\div 10 \text{ A.}  \text{Cd}(8)(10) \div 10 \text{ A.}$	do.	olatinum.	to 24.5 27 to 27	18.5	25 to 30 27.5 to 26	to 18.6 19.5 to 19.9	2700 4050	110.88 107.05	22.8	25 27.5	18-82 19-92	2617.4 2649.0	143.42 143.41	824.89 824.77	0.17387
74.	W. J. B.	15h. 10.8.07. 15h. 12·8.07. 12h.	Na <sub>2</sub> SO <sub>4</sub> 30 °/ <sub>0</sub> .	$Cd(8)(9)(10) \div 10 A$ .	2 0.0.	3 sq. cm. bright platinum.	16.6 to 16.8 13.6 to 16.5   16.6 to 15.2   21.4 to 22.5   20 5 to 24.5	194	27.5 to ?	12.5 to 12.5   18.2 to 19.7   18.2 to 18.6	2700	108.64	22 6	26.2	19.69	2638 9 20	143.45	824.87	0.17391 0.1
70.	R. A. L.	15h.	7 10 °/ <sub>0</sub> .	n parallel).	do.	3 sq. c	16.6 to 15.2	12.8	23 to $27.5$	12.5 to 12.5	2025	116.28	15.0	23	12.44	2516.2	143.48	825.09	0.17390
.69	B. A. L.	5.7.07. 14h.	$K_2 Cr_2 O_7 10 \%$	(10л & 10ві	2 c.c.   do.		13.6 to 16.5	11.8	22 to 25.5	11.3 to 12.1	2025	116 44	16.5	22	12.20	2513.2	143.50	825.12	0.17391
55.	R. A. L.	15h.   1.7.07. 15h.   5.7.07. 14h.	e. water.	Cd(2)(3)÷	) :	n.	16.6 to 16.8	15	29 to 35·5	15.0 to 14.6	2025	114:51	16.8	29	14.62	2548·3	143.46	825.02	0.17389
52.	R. A. L.	15h.	$30~{\rm g.~Na_2SO_4}.10{\rm H_2O}$ in $100~{\rm c.c.}$ water.	Od cells $(1)(2)$ & $(3) \div \text{res. } 10$ A. $  \text{Cd}(2)(3) \div (10$ A & $10$ B in parallel).	)	1 eq. cm. bright platinum.	17.6	15.8	23 to 28	15.2 to 15.6	2700	113.37	17.6	23	15.80	2568.8	143.53	825.0	0.17398
51,	R. A. L.	28.6.07, 10h.	30 g. Na <sub>2</sub> SO <sub>4</sub>	Od cells (1)(2)	)	1 eq. c)	14	11.5	24	13.2	2700	114.00	16.2	23	14.20	2546.4	143.53	825.1	0.17396
No. of experiment	Observer	Date	Electrolyte		Waste space	Electrodes	Temp. air	" Cd cells	" coulometer	" water-jacket.	Time (sec.)	Barometer		T. coulometer	`:	Weight of mercury	Reduced volume	Quantity of electricity	Result

Table I. (continued).

No. of experiment	80.	85.	86.	87.	88.	.68	.06	91.
	R. A. L.	R. A. L.	W. J.	W. J.	W. J.	W. J.	W. J.	R. A. L.
Date	17.9.07. 15h.	23.9.07. 12h.	24.9.07. 15h.	24.9.07. 16h.	24.9.07. 17h.	23.9.07. 12h, 24.9.07. 15h, 24.9.07. 16h, 24.9.07. 17h, 1.10.07. 15h, 1.10.07. 16h,	1.10.07. 16h.	2.10.07. 15h.
-	$Na_2SO_4 30 \%$		10 %	10 % Na <sub>2</sub> SO <sub>4</sub> .			10 % K2Cr2O7.	7.
Current	Cd (e)	$\operatorname{Cd}\left(\mathbf{s}\right)\left(10\right)\div\left(10\mathrm{A}\ \&\ 10\mathrm{B}\ \mathrm{in\ parallel}\right).$	10 B in par	allel).	Cd (8)	$Cd(8)(9)(10) \div 10 \text{ Å \& } 10 \text{ B.}$	1	$Od(8)(10) \div 10 A.$
Waste space	3 c.c.	3½ c.c.	5 c.c.   do.	do.	do. (	5 c.c.	do.	) op
Electrodes			3 sq.	cm. br	sq. cm. bright platinum.	tinum.		
Temp. air	19·2 to 19·5	16 to 16	18·2 to 19·0	19.0 to 19.2	18.2 to 19.0   19.0 to 19.2   19.2 to 19.0	22 to 25	23 to 26	22 to 23
Cd cells	16.3	12.3	16.7	17.5	18.0	20.7	21.1	20.5 to 20.8
coulometer	26 to 33	26 to 36	26 to 32	28.5 to 32	42.5 to 45	33.5 to 38	36 to 38	25.5 to 25
water-jacket.	16.9 to 17.4	14.5 to 14.0	15.7 to 15.7	14.5 to 14.0 15.7 to 15.7 16.0 to 15.8	15.8 to 15.6	20·2 to 20·3	20.2 to 19.9	20.5 to 19.4
Time (sec.)	2025	2025	2025	2025	1350	1380	1380	4050
Barometer	114.67	116.94	115.73	115.64	115.59	113.83	113.84	111.72
T. barometer	18.4	15.3	19.2	19.5	19.1	21.6	21.4	20.5
T. coulometer	26	26	26	28.5	42.8	33.2	33.5	24.0
T. gas	17.72	14.08	15.62	15.84	15.60	20.50	19.90	19.40
Weight of mercury	2587.3	2532.2	2557.7	$2560 \cdot 1$	2558.0	2686.0	2875.8	2621.9
Reduced volume	143.53	143.52	143.55	143.51	143.55	146.70	146.61	143.55
Quantity of electricity	824.98	825·10	824.97	824.95	824.93	843·18	843.17	824.83
Result	0.17398	0.17394	0.17401	0.17396	0.17401	0.17398	0.17388	0.17404

LVIII. Inverse Interpolation by Means of a Reversed Series. By C. E. Van Orstrand\*.

THE formulas developed by Newton, Bessel, and Stirling for the direct interpolation of a value of a function from values tabulated at equal intervals of the argument, are considered to be among the most important of their contributions to the science of applied mathematics. The converse problem, that of finding the argument when a value of the function is given, although of about equal importance, seems not to have received the thorough treatment which mathematicians have given to the subject of direct interpolation. Apart from methods applicable only to special cases, there are two general methods t now in use which are to a certain extent satisfactory. Each of the methods is in reality based upon the same principle—that of diminishing the interval of interpo-In the one case this is accomplished by computing values of the function at equal intervals of the argument for values preceding and following the required value. interval of the new series of tabular values is sufficiently small, the correct argument can be found by taking second differences into account. In the second case, the function and its first and second derivatives are computed for a value of the argument (n) true to the nearest tenth of a unit. is then generally sufficient to write the interpolation formula as a Taylor's series involving only the first and second derivatives. The correction to the approximate value of the argument is then found by reverting this series of two terms. Each of the methods has the serious disadvantage of being a tentative process, and neither of them provides a satisfactory check on the computation, without the aid of additional quantities.

As a means of avoiding the difficulties noted above, it is desirable to call attention to the use which may be made of a reverted series as a formula for inverse interpolation. To derive this formula, let the tabular values of the function  $(F_{-3}, F_{-2}, \ldots)$  and its successive differences (the a's, b's  $\ldots$ ) be represented by the following schedule:—

\* Communicated by the Author.

<sup>†</sup> Rice, 'Theory and Practice of Interpolation,' pp. 192-5.

T	F(T)	Δ'	Δ''	Δ'''	$\Delta^{IV}$	Δv
$t - 3\omega$ $t - 2\omega$ $t - \omega$ $t$ $t + \omega$ $t + 2\omega$ $t + 3\omega$	F-3 F-2 F-1 F <sub>0</sub> F <sub>1</sub> F <sub>2</sub> F <sub>3</sub>	$a_{-3}$ $a_{-2}$ $a_{-1}$ $a_{1}$ $a_{2}$ $a_{3}$	$b_{-2}$ $b_{-1}$ $b_{0}$ $b_{1}$	$c_{-2}$ $c_{-1}$ $c_{1}$ $c_{2}$	$d_{-1}$ $d_0$ $d_1$	$e_{-1}$ $e_{1}$

Put also

$$a = \frac{1}{2}(a_1 + a_{-1}) \qquad a' = a - \frac{c}{6} + \frac{e}{30}$$

$$e = \frac{1}{2}(c_1 + c_{-1}) \qquad b' = \frac{b_0}{2} - \frac{d_0}{24}$$

$$e = \frac{1}{2}(e_1 + e_{-1}) \qquad c' = \frac{c}{6} - \frac{e}{24}$$

$$\Delta F = F_n - F_0 \qquad d' = \frac{d_0}{24}$$

$$e' = \frac{e}{120}$$

Then, using Stirling's expression for the successive derivatives, because of their simplicity and rapid convergence, and writing the interpolation formula as a Taylor's series,

$$\Delta \mathbf{F} = a'n + b'n^2 + c'n^3 + d'n^4 + e'n^5 + \dots$$
 (1)

The solution of the problem consists in finding the value of n when  $\Delta F$ , a', b', c', ... are given. To accomplish this, we revert equation (1) by means of the usual method of equating coefficients, or by means of the expression obtained by Professor McMahon for the general term of a reverted series\*, and obtain

$$n = \frac{\Delta F}{a'} - \frac{b'}{a'} \left(\frac{\Delta F}{a'}\right)^2 + \left[2\left(\frac{b'}{a'}\right)^2 - \frac{c'}{a'}\right] \left(\frac{\Delta F}{a'}\right)^3 + \left[5\frac{b}{a'}\frac{c'}{a'} - \frac{d'}{a'} - 5\left(\frac{b'}{a'}\right)^3\right] \left(\frac{\Delta F}{a'}\right)^4 + \left[3\left(\frac{c'}{a'}\right)^2 + 6\frac{b'}{a'}\frac{d'}{a'} - \frac{e'}{a'} - 21\left(\frac{b'}{a'}\right)^2\frac{c'}{a'} + 14\left(\frac{b'}{a'}\right)^4\right] \left(\frac{\Delta F}{a'}\right)^5 + \dots (2)$$

\* Bull. Am. Math. Soc. iii. p. 170 (1893-1894).

Equation (2) may be put into a more convenient form for computation by rearranging the terms and putting  $n_1 = \Delta F \div a'$  and  $r = n_1 \div a'$ . Then

$$n = n_1 + \left[ -rb' + 2(rb')^2 - 5(rb')^3 + 14(rb')^4 \right] n_1$$

$$+ \left[ rc' (-1 + 5rb' - 21(rb')^2 \right] n_1^2$$

$$+ \left[ rd' (-1 + 6rb') + 3(rc')^2 \right] n_1^3$$

$$+ \left[ -re' \right] n_1^4 + \dots$$
(3)

Now substitute

$$\begin{split} f_1 &= -rb' + 2 \; (rb')^2 - 5 \; (rb')^3 + 14 \; (rb')^4 \\ f_2 &= rc' \big[ -1 + 5 \; rb' - 21 \; (rb')^2 \big] \\ f_3 &= rd' \big[ -1 + 6 \; rb' \big] + 3 \; (rc')^2 \\ f_4 &= -re' \end{split}$$

in (3), and the equation for inverse interpolation, inclusive of fifth differences, is

$$n = n_1 + f_1 n_1 + f_2 n_1^2 + f_3 n_1^3 + f_4 n_1^4$$
. (4)

For backward interpolation  $n_1$  is negative. A slightly different form of (4) convenient for logarithmic computation is

 $n = n_1 + f_1 n_1 + rc' f_2' n_1^2 + rd' f_3' n_1^3 + 3(rc')^2 n_1^3 + f_4 n_1^4 \dots$  (5) in which

$$f_2' = -1 + 5 \ rb' - 21 \ (rb')^2$$
  
 $f_3' = -1 + 6 \ rb'$ .

The expressions for the f's, as obtained by developing the reverted series to the same order of powers as the given series, are represented by the following groups, according as each series terminates with the second, third, or fourth power:

$$f_1 \equiv -rb' \equiv -rb' + 2 (rb')^2 \equiv -rb' + 2 (rb')^2 - 5 (rb')^3$$

$$f_2 \equiv \qquad \equiv -rc' \qquad \equiv rc'(-1 + 5rb')$$

$$f_3 \equiv \qquad \equiv -rd'.$$

Analytically, there are an infinite number of the f's and each contains an infinite number of terms. The number of terms required in any particular reversion is easily ascertained from the data. As a complete formula for inverse interpolation, applicable in all cases, the reversed series is unfortunately not always sufficiently convergent when a limited number of terms is used. However, the most important applications of reversion obtain when the numerical magnitudes of the successive orders of differences gradually diminish. It will be found for such functions that rb' < 0.1, and since  $n < \frac{1}{2}$ , the

doubly infinite series will always converge\*. The cases in which the series fails to converge with sufficient rapidity are therefore exceptional and are easily discovered. In fact it is only necessary to see if the terms at the end of each horizontal series, such as  $14 \ (rb')^4 n_1$ ,  $21 \ rc' \ (rb')^2 n^2$ , ..., are small in comparison with  $n_1$ .

The quantities (a'b'c'd'e') are easily computed when the first derivatives are tabulated. Representing the functional values, the first derivatives, and the successive differences of

the first derivatives by the scheme:

т	F(T)	ωF'	Δ'	Δ''	Δ'''	Διν
$t - 3\omega$ $t - 2\omega$ $t - \omega$ $t$ $t + \omega$ $t + 2\omega$ $t + 3\omega$	$F_{-3}$ $F_{-2}$ $F_{-1}$ $F_{0}$ $F_{1}$ $F_{2}$ $F_{3}$	$a_{-3}$ $a_{-2}$ $a_{-1}$ $a_{0}$ $a_{1}$ $a_{2}$	$\beta_{-3}$ $\beta_{-2}$ $\beta_{-1}$ $\beta_{1}$ $\beta_{2}$ $\beta_{3}$	$egin{array}{cccc} \gamma-2 & & & & & & & & & & & & & & & & & & &$	$\hat{c}_{-2}$ $\hat{c}_{-1}$ $\hat{c}_{1}$	$\epsilon_{-1}$ $\epsilon_{_0}$

these auxiliary quantities are represented by the simple forms:—

$$\begin{aligned} a' &= \alpha_0 \\ b' &= \frac{\beta}{2} - \frac{\delta}{12} \\ c' &= \frac{\gamma_0}{6} - \frac{\epsilon_0}{72} \\ d' &= \frac{\delta}{24} \\ e' &= \frac{\epsilon_0}{120} \end{aligned} \qquad \beta = \frac{1}{2}(\beta_1 + \beta_{-1}) = \beta_1 - \frac{\gamma_0}{2}$$

when Stirling's formulas for the successive derivatives are used. Evidently,

$$b' = \frac{\omega^2 \mathbf{F}_0''}{2}; \ e' = \frac{\omega^3 \mathbf{F}_0'''}{6}; \ d' = \frac{\omega^4 \mathbf{F}_0^{iv}}{24}; \ e' = \frac{\omega^5 \mathbf{F}_0^{v}}{120}.$$

The computation of  $a', b', c', d', e' \dots$  can be checked in various ways. In general it is quite sufficient to duplicate the work. An independent check is of course obtained by computing

<sup>\*</sup> Harkness & Morley, 'Treatise on Theory of Functions,' p. 116.

the derivatives from the formulas of either Newton or Bessel, preferably the latter for arguments other than at the beginning

or end of a series of tabular values.

As an application of formula (4) let it be required to find the interpolation interval (n) from the following tabular values of the function and its differences, when the logarithm of Mercury's distance from the Earth equals  $F_n = 9.7968280$ .

We take from the table,

$$\begin{aligned} \mathbf{F}_0 &= 9.7905482, \\ a &= \frac{1}{2} \left( a_1 + a_{-1} \right) = + 144461.5 \\ b_0 &= + 15725 \\ c &= \frac{1}{2} \left( c_1 + c_{-1} \right) = - 4137.5 \\ d_0 &= + 457 \\ e &= \frac{1}{2} \left( e_1 + e_{-1} \right) = + 105.0 \end{aligned}$$

and then compute,

$$b' = \frac{b_0}{2} - \frac{d_0}{24} \qquad = + \quad 7843 \cdot 5 \qquad 3 \cdot 894510 \qquad rb' = + 0 \cdot 233773$$

$$c' = \frac{c}{6} - \frac{e}{24} \qquad = - \quad 693 \cdot 9 \qquad 2 \cdot 84130^n \qquad rc' = -0 \cdot 0020681$$

$$d' = \frac{d_0}{24} \qquad = + \quad 19 \cdot 0 \qquad 1 \cdot 2788 \qquad rd' = + 0 \cdot 0000566$$

$$e' = \frac{e}{120} \qquad = + \quad 0 \cdot 9 \qquad 9 \cdot 954_{-10} \qquad re' = + 0 \cdot 0000027$$

$$\Delta F = F_n - F_0 \qquad = + \quad 62798 \cdot 0 \qquad 4 \cdot 7979458 \qquad f_1 = -0 \cdot 0223441$$

$$a' = a - \frac{c}{6} + \frac{e}{30} = + 145154 \cdot 6 \qquad 5 \cdot 1618308 \qquad f_2 = + 0 \cdot 0018500$$

$$n_1 = \Delta F \div a' \qquad = \qquad 9 \cdot 6361150_{-10} \qquad f_3 = + 0 \cdot 0000359$$

$$r = n_1 \div a' \qquad = \qquad 4 \cdot 4742842_{-10} \qquad f_4 = -0 \cdot 0000027.$$

Substituting in equation (4) we compute n; then substituting n in equation (1) we compute  $\Delta F$  as a check. Thus,

$n_1 = +0.4326284$	a'n = +61444.7
$f_1 n_1 = -0.0096667$	$b'n^2 = + 1405.4$
$f_2 n_1^2 = +0.0003463$	$c'n^3 = -$ 52.6
$t_3^3 n_1^3 = -0.0000029$	$d'n^4 = + 0.6$
$f_4 n_1^4 = -0.0000001$	$e'n^5 = 0.0$
$n = \Sigma = +0.423305$	$\Delta F = \Sigma = + 62798 \cdot 1.$

By means of the second method of inverse interpolation previously explained, Rice\* finds n=0.423303. This discrepancy is due to neglecting units in the seventh decimal place. The value of  $\Delta F$  computed from this value of n and Stirling's derivatives is  $\Delta F = 62797.7$ .

There are a great number of tabulated functions in which second differences are approximately constant and in which the term  $2n_1(rb')^2$  is negligible. In such cases the following rule applies: Divide the increment of the function  $(\Delta F)$  by the mean of the first differences  $(a_1 + \frac{1}{2}b_0)$ , and likewise divide this quotient  $(n_1)$  by the same quantity; then the product of these two quotients  $(n_1r)$  and one-half the second difference  $(\frac{1}{2}b_0)$  is the correction to be applied algebraically to the first quotient  $(n_1)$  in order to obtain the required interpolation interval (n). The algebraic signs of the quantities need not be taken into account; for it is plain that if the numerical values of the first differences are increasing, the quotient  $(n_1)$ is too large and the correction is therefore negative, while if the numerical values of the first differences are decreasing, the value of  $n_1$  is too small and the correction is positive. This method is very convenient when the numbers are so large as to require the use of a logarithm table in making the interpolation. For example, let it be required to find  $\theta$  from Vega's ten-place table when  $\log \sin \theta = 8.9107867247$ .

The tabular values are as follows:—

θ. 4° 40" 0"		$\Delta'$ .	$\Delta^{_{!}}{}'.$
10	910 6617 247	+2578594	-1537
20	910 9194 304	2577 057	<b>-1538</b>
30	·911 1769 823	+2575 519	

The quantity to be computed is

$$n = n_1 - rb'n_1.$$

<sup>\*</sup> Loc. cit. p. 195.

We disregard the algebraic sign of the last term, for a mere inspection of the first differences suffices to show that the correction to  $n_1$  is positive. Following is the computation:—

$\mathbf{F}_n =$		8.910 7867 247		
$F_0 =$		8.910 6617 247		
$\Delta F =$		+1250 000	6.096 9100	
$a' = a_1 +$	b' =	+2577 825	6.411 2534	
		0.484 9049	9.685 6566-10	
$r = n_1 \div$	a'=		3.2744-10	
$b' = \frac{b_0}{2}$	=	<b>-768</b>	2.8854	Check.
$n_1 r b' =$		+0.000 0701	5.8455	$a'n = 1250 \ 181$
n =		0.484 9750	9.6857193	$b'n^2 = -181$
$\theta =$	4° 40	14''.84975		$\Delta F = 1250'000$

The value of the term  $2n_1(rb')^2$  is  $2 \times 10^{-8}$ , a negligible quantity. The formula here suggested will frequently be applicable when the differences are small numbers. computation may be made by actual multiplication and division; but in general, logarithmic computation requires less labour. In either case, the method just explained is about as easy of application as any other, except that in miscellaneous computations, some care must be exercised to see that the term  $2n_1(rb')^2$  may be omitted. On the other hand, if the higher differences need be taken into account, the complete formula has the important advantage of putting into evidence the terms necessary to obtain a required degree of accuracy. Thus, although third differences occur in that portion of Vega's ten-place table of the logarithmic sines for arguments = or  $> 2^{\circ}$ , the terms in rc' are negligible and the maximum value of  $2n_1(rb')^2$ , which occurs in the immediate vicinity of 2°, is five units in the seventh decimal place. Consequently, the correction to the simple formula

$$n\!=\!n_1\!-\!n_1rb'$$

is so small that it may be omitted except when extreme accuracy is required for arguments a little greater than 2°.

A problem of frequent occurrence in many branches of applied science is the reversion of an empirical formula expressed in the form of a power series. Since the relation is given in the form (1), it is only necessary to substitute in (3) to obtain the value of the argument or independent variable. As an illustration, find the temperature of quick-silver when its volume is 1 01825409. The empirical formula given by Chappuis \* expressing the increase of volume of

quicksilver as a function of the temperature, for temperatures ranging from 0° to 100° C., may be written

$$\Delta v = [6.259332_{-10}]t - [1.470008_{-10}]t^2 + [0.059041_{-10}]t^3.$$

Arranging the computation as before,

$$b' = 1.470008_{-10} rb' = 7.212704_{n-10}$$

$$c' = 0.059041_{-10} rc' = 5.801737_{-10}$$

$$\Delta F = \Delta v = 8.261360_{-10} f_1 = 7.21412_n$$

$$a' = 6.259332_{-10} f_2 = 5.80174_{-10}$$

$$t_1 = t_1 = 2.002028 t_1 = 100.4681$$

$$r = 5.742696 f_1t_1 = + 0.1645$$

$$f_2t_1^2 = -0.6394$$

$$t = \Sigma = 100^{\circ}.007 \text{ C}$$

Instances may arise where it will be more convenient on account of the relative magnitude of the quantities to compute the coefficients of equation (2) instead of the auxiliary quantities  $f_1, f_2, f_3, \ldots$  Written in this form, the inverse of Chappuis' equation is

$$t = \lceil 3.740668 \rceil \Delta v + \lceil 2.692012 \rceil (\Delta v)^2 - \lceil 5.021349 \rceil (\Delta v)^3$$
. (a)

Sometimes, however, the inverted series converges so slowly as to be useless. Probably the best manner of handling such tabulated data or empirical relations is to select or compute n values of the function corresponding to n values of the independent variable and substitute in an equation of the form,

$$t = A_1(\Delta v) + A_2(\Delta v)^2 + A_3(\Delta v)^3 + \dots + A_n(\Delta v)^n$$

and then evaluate the n unknowns  $(A_1, A_2, \ldots A_n)$  by solving the n linear equations. Proceeding in this manner and using the values

$$t = 30^{\circ} \text{ C.}$$
  $\Delta v = \begin{bmatrix} 7.736488_{-10} \end{bmatrix}$   
 $t = 60^{\circ} \text{ C.}$   $\Delta v = \begin{bmatrix} 8.038045_{-10} \end{bmatrix}$   
 $t = 90^{\circ} \text{ C.}$   $\Delta v = \begin{bmatrix} 8.215155_{-10} \end{bmatrix}$ 

there results for the last equation,

$$t = [3.740678]\Delta v + [2.655719](\Delta v)^{2} - [5.009834](\Delta v)^{3}.$$
 (b)

The coefficients of (a) differ slightly from those of (b). Substituting  $\Delta v = 0.0182541$ , the values found for t are

$$t_a = 100^{\circ} \cdot 007 \text{ C.},$$
  
 $t_b = 99^{\circ} \cdot 999 \text{ C.}$ 

and

The value  $t=100^{\circ}.007$  C. is the same as found from equation (3), the modified form of the general formula for inverse interpolation. Either of these three methods is sufficiently accurate for this problem. The last two methods are

to be used in preference to the first when a great number of values is to be interpolated. In the many instances in which only one or two values are to be obtained, the first method is the most convenient. Functions determined by any of the preceding methods may not of course be very reliable for extrapolation. The last formula, for example, is applicable between the limits  $30^{\circ}$  and  $90^{\circ}$ , but is uncertain for values of  $t < 30^{\circ}$  and  $>90^{\circ}$ .

It is desirable to ascertain if some other arrangement of the terms of the reverted series would facilitate computation. The numerous possible combinations of the quantities are best exhibited by again making use of Professor McMahon's expression for the general term of a reverted series. Putting

$$b_1 = \frac{b'}{a'};$$
  $b_2 = \frac{c'}{a'};$   $b_3 = \frac{d'}{a'};$   $b_4 = \frac{e'}{a'}; \ldots,$ 

the (m-1)th term of the reverted series may be written

$$m(m+1)(m+2)\ldots(p+q+\ldots(m-2))\Big[\sum \frac{b_i^p}{p:q:}\frac{b_i^q}{q:}\Big]n^{m-1},$$

in which the exponents and subscripts are subject to the condition  $pi+qj+\ldots=m-2$ .

Giving m successive values, say from 3 to 8, we easily find the terms containing all possible combinations of  $b_1^p b_2^q \dots b_6^u$ . They are

m=3  $b_1$ ,

4  $b_1^2$   $b_2$ 

 $\begin{bmatrix} 1 & 1 & 1 & 1 \\ 5 & b_1^3 & b_1 & b_2 & b_3 \end{bmatrix}$ 

 $6 \quad b_1^4 \quad b_1^2 b_2 \quad b_1 \ b_3 \quad b_2 b_2 \qquad b_4$ 

7  $b_1^5$   $b_1^8$   $b_2$   $b_1^2$   $b_3$   $b_3$   $b_2$   $b_1$   $b_4$   $b_5$ 

 $8 \quad b_1^{\ 6} \quad b_1^{\ 4} \ b_2 \quad b_1^{\ 3} \ b_3 \quad b_4 \ b_2 \quad b_1^{\ 2} \ b_4 \quad b_1 b_5 \quad b_1 b_2 b_3 \quad b_3^{\ 2} \quad b_2^{\ 3} \quad b_6.$ 

Each term is of weight m-2. There are two combinations of the terms of nearly complete symmetry in which functions of the same quantities appear in a form suitable for computation. Thus, assuming that the given series terminates with the fifth power, one arrangement of the terms is

$$\begin{vmatrix}
+b_{1}+b_{1}^{2}+b_{1}^{3}+b_{1}^{4}+b_{1}^{5}+\dots \\
+b_{2}[1+b_{1}+b_{1}^{2}+b_{1}^{3}+\dots] \\
+b_{3}[1+b_{1}+b_{1}^{2}+b_{1}^{3}+\dots] \\
+b_{4}[1+b_{1}+b_{1}^{2}+\dots] \\
+b_{5}[1+b_{1}+\dots] \\
+\dots\dots,
\end{vmatrix}$$
(1)

and another is

$$\begin{vmatrix}
+b_1+b_2+b_3+b_4+\ldots \\
+b_1[b_1+b_2+b_3+\ldots] \\
+b_1^2[b_1+b_2+b_3+\ldots] \\
+b_1^3[b_1+b_2+b_3+\ldots] + \ldots b_2[b_2+b_3+\ldots]
\end{vmatrix}$$
(2)

The elements have been selected firstly with respect to the verticals, and secondly with respect to the diagonals. Of other approximately homogeneous and symmetrical combinations there are none. Group (1) has been used in equation (3). Group (2) gives the formula

$$n = n_{1} + \frac{b'}{a'} n_{1}^{2} \left[ -1 - \frac{c'}{b'} n_{1} - \frac{d'}{b'} n_{1}^{2} - \frac{e'}{b'} n_{1}^{3} - \dots \right]$$

$$+ \left( \frac{b'}{a'} \right)^{2} n_{1}^{3} \left[ +2 + 5 \frac{c'}{b'} n_{1} + 6 \frac{d'}{b'} n_{1}^{2} + \dots + 3 \left( \frac{c'}{b'} \right)^{2} n_{1}^{2} + \dots \right]$$

$$+ \left( \frac{b'}{a'} \right)^{3} n_{1}^{4} \left[ -5 - 21 \frac{c'}{b'} n_{1} - \dots \right]$$

$$+ \left( \frac{b'}{a'} \right)^{4} n_{1}^{5} \left[ +14 + \dots \right],$$

or

$$n = n_1 + f_1 \left(\frac{b'}{a'}\right) n_1^2 + f_2 \left(\frac{b'}{a'}\right)^2 n_1^3 + f_3 \left(\frac{b'}{a'}\right)^3 n_1^4 + f_4 \left(\frac{b'}{a'}\right)^4 n_1^5. \quad (6)$$

As in equation (3), symmetry fails in the term  $b_2^2 n_1^5$ . The functions within the brackets are not dependent upon a single quantity as in the other formula, but their evaluation involves only a summation of simple functions of the same variables. The distribution of algebraic signs is unique.

Computing again the interpolation interval (n) from the data of the first problem, there results:

$$\log\left(\frac{b'}{a'}\right)n_1^2 = 8.004909_{-10} \qquad n_1 = +0.4326284$$

$$\log\left(\frac{c'}{b'}\right)n_1^2 = 8.58290_{n-10} \qquad f_1\left(\frac{b'}{a'}\right)n_1^2 = -0.0097313$$

$$\log\left(\frac{c'}{b'}\right)^2n_1^2 = 7.16580_{-10} \qquad f_2\left(\frac{b'}{a'}\right)^2n_1^3 = +0.0004293$$

$$\log\left(\frac{d'}{b'}\right)n_1^2 = 6.6565_{-10} \qquad f_3\left(\frac{b'}{a'}\right)^3n_1^4 = -0.0000232$$

$$\log\left(\frac{e'}{b'}\right)n_1^3 = 4.967_{-10} \qquad f_4\left(\frac{b'}{a'}\right)^4n_1^5 = +0.0000018$$

$$n = \Sigma = +0.423305,$$

the value obtained by the first method.

The reversed series necessarily involves the quotients, powers, and products of the differences, and for this reason is difficult of computation. This difficulty is largely overcome in the above formulas by taking advantage of the homogeneity of the reverted series, and expressing certain factors, the f's, as functions of the same quantities. If the values of the f's, or preferably their logarithms, were tabulated, the labour involved in inverse interpolation would be not much greater than that of direct interpolation; for each of the terms in (4), (5), or (6) would then be given in the form of simple product expressions suitable for logarithmic computation. This method has the further advantage of being straightforward; and in so far as the reversion of the series is concerned, a check is provided without the introduction of any new quantities by the substitution of n in equation (1).

The possibility of using the reversed series as a formula for inverse interpolation was suggested to me by Dr. George F. Becker of the U.S. Geological Survey, with whom I have cooperated in preparing a volume of mathematical tables \* entitled 'Tables of Hyperbolic Functions,' and now in course of publication by the Smithsonian Institution of Washington, D.C. The formulas here suggested have been used to a certain extent in the preparation of these tables.

Washington, D.C., February 1908.

LIX. On the Different Kinds of  $\gamma$  Rays of Radium, and the Secondary  $\gamma$  Rays which they produce. By R. D. KLEEMAN, B.A., B.Sc., 1851 Exhibition Research Scholar of the University of Adelaide, and Research Student of Emmanuel College; Emmanuel College, Cambridge  $\dagger$ .

 $\mathbf{I}^{\mathrm{N}}$  a paper published in the Philosophical Magazine‡ the writer showed that part of the  $\gamma$  radiation of radium could be approximately divided into three groups of rays. Each of these groups of rays is selectively absorbed by one

† Communicated by Prof. J. J. Thomson, F.R.S.

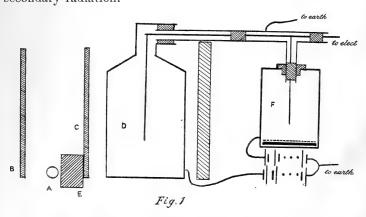
† Phil. Mag. Nov. 1907, p. 618.

<sup>\*</sup> In this volume are tabulated the natural and logarithmic hyperbolic sines, cosines, tangents, and cotangents to five places; the natural and logarithmic circular sines and cosines to five places; the ascending and descending exponential to seven significant figures with  $\log_{10}e^{\mu}$  to seven places; the natural logarithms of the integral numbers from 1 to 1000 to five places; the gudermannian to seven places and the corresponding angular equivalents; the anti-gudermannian to hundredths of a second; and other tables of minor importance. The arguments for the most part advance by ten-thousandths from 0 to 0·1, by thousandths from 0·1 to 3·0, and by hundredths from 3·0 to 6·0.

of three groups of substances. Thus, if the three groups of rays be denoted by A, B, and C, then the group A is better absorbed by one of the three groups of substances than either of the groups B and C, and the group B better absorbed by one of the other groups of substances than either of the groups A and C, and lastly the group of rays C is better absorbed by the remaining group of substances than either of the groups of rays A and B. To give an illustration, the ratio of the secondary cathode radiation from lead to that from zinc is decreased if the  $\gamma$  rays are passed through a thick screen of lead before falling on the radiators, showing that the rays producing the larger part of the radiation from zinc are decreased in a less proportion by the lead screen than the rays producing the larger part of the radiation from lead.

It became of interest, therefore, to investigate the properties of the secondary  $\gamma$  rays from different substances exposed to the  $\gamma$  rays of radium, and to compare their properties with those of the primary rays. Moreover, it was thought that such an investigation might lead to an indirect confirmation of the above result. The experiments described in this paper were accordingly undertaken.

It appeared from the experiments described in the paper mentioned, that the amount of secondary  $\gamma$  radiation, as measured by its ionizing power, is small in comparison with that of the incident primary radiation. It was necessary, therefore, to design a sensitive apparatus for measuring the secondary radiation.



A vertical section of the apparatus used is shown in fig. 1. A is a quantity of radium (about 30 mgrs.) in a glass tube surrounded by lead sheeting 2 mm. thick to cut off the

 $\beta$  rays. The  $\gamma$  rays fell in part on the radiator B, which in consequence emitted secondary  $\beta$  and secondary  $\gamma$  rays. Some of the secondary rays penetrated into the ionization chamber D, ionizing the air that it contained. The selective absorption of the secondary  $\gamma$  rays was investigated by placing successively screens of different substances at C, and measuring in each case the ionization in the chamber D, the ionization in the chamber being produced by the secondary rays not absorbed by the screen. By using radiators and screens of different substances the properties of the secondary radiation from different substances could thus be investigated. The screen served also to screen the ionization-chamber from the secondary  $\beta$  rays emitted by the radiator B. This was necessary since the ionization-chamber was made of thin

by the  $\beta$  rays. The object of having the ionization-chamber of thin material was to introduce as little absorption of the secondary  $\gamma$  rays as possible other than that due to the screen. The screen C and the ionization-chamber were screened from the action of the primary rays by the lead block E 16.5 cm.

sheet iron which would have been penetrated to some extent

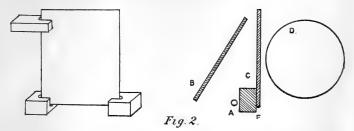
long, 9.5 cm. broad, and 5.5 cm. thick.

But since the  $\gamma$  rays possess great penetrating power, an object can be screened approximately only from the action of  $\gamma$  rays, and the leak in the ionization-chamber was therefore caused in part by the primary  $\gamma$  rays which penetrated the lead block. It was therefore found convenient to partially compensate the leak in the chamber by a leak in the opposite direction in another chamber F. The air in this chamber was ionized by a layer of uranium oxide, and the chamber placed at a distance of one metre from the radiator B and screened from its secondary  $\gamma$  rays by a lead plate 1.5 cm. thick. The leak in the chamber was therefore not affected when the radiator was replaced by another, and was therefore constant. The chamber F was connected to a negative potential of 200 volts, while the chamber D was connected to a positive potential of the same magnitude.

On the right-hand side of fig. 2 a horizontal section of part of the apparatus is shown. It will be seen that the radiator was placed so that it made an angle of about 45° with the screen. This was done because the amount of radiation received from the radium was greatest in this position.

On the left-hand side of the figure the arrangement is shown by means of which the radiator or screen was kept in a fixed position. It consisted in each case of three fixed blocks of wood provided with slits whose width was slightly greater than the thickness of the radiator or screen. Both radiator and screen were kept in a fixed position by being

held to one of the sides of each slit by means of a wedge. Therefore, when one of them was removed and again replaced, it always occupied its previous position.



In order to obtain as large a leak as possible, the radiator B and the ionization-chamber D were made as large as was possible without causing any inconvenience. The leak in D, it will be observed, is approximately proportional to the product of the capacity of the ionization-chamber and the area of one side of the radiator, if the thickness of the radiator is kept constant. The length and breadth of each of the plates actually used as radiators were 28 and 24 cm. respectively. The ionization-chamber was of a cylindrical shape, its diameter was 18 cm., and its height approximately 20 cm.

The leak in the chamber D, as has already been pointed out, is partly due to the direct action of the  $\gamma$  rays penetrating the lead block E. If we denote by N the leak per second due to these primary rays, and by M the leak due to the secondary rays, then the leak when the radiator is in position is given by (N+M). By observing the leak with no radiator we obtain the value of N. The value of M is

then obtained by subtracting N from (N+M).

In practice, the leak N or (N+M) was obtained by observing the time taken by the electrometer-needle to reach a given deflexion. The deflexion for a given time could then be easily calculated. In this manner, the error due to the change of capacity of the electrometer with deflexion of needle was obviated. It will be observed, however, that if N is much greater than M (in these experiments this was the case), the times required to obtain a given deflexion when observing the leaks N and (N+M) would differ from one another by much less than the time of either leak. The possible error that is attached to the value of this difference is therefore large; and the error that is attached to the value of M, which depends on this difference, is therefore also large. This defect in the method was obviated by the use of the uranium chamber. The leak due to the primary

rays could be wholly or partially compensated by a leak in the opposite direction in the uranium chamber, and the difference in the times of leak thereby rendered as large as convenient.

The compensation was, however, rendered only partial, this affording a method of eliminating the loss of leak due to leakage over the insulation, and leakage in the screening tubing due to imperfect shielding from the  $\gamma$  rays. Thus, if the times required to obtain a given deflexion with the leaks N and (N+M) be measured, the leaks for a given time (not corrected for loss of leak) can be calculated. calculated leaks be denoted by  $N_1$  and  $(N_1 + M_1)$ . Then the true value of M unaffected by leakage is given by subtracting  $N_1$  from  $(N_1 + M_1)$ , as will now be shown. the system is charged, the loss of charge at any instant is approximately proportional to the deflexion of the electrometer-needle. Therefore the loss of leak for a time dt is DA. dt, where D is the deflexion of the electrometer-needle and A is a constant. If n denote the leak per second if there were no loss of leak, then, since the loss of leak is small in comparison with the leak, D=tn approximately. If the leak be taken for a time  $t_1$ , the loss of leak is approximately equal to  $\int_{0}^{t_1} tnA \cdot dt$ , that is to  $t_1^2An/2$ . If  $t_1$  denote

the time required to obtain some given deflexion  $D_1$ ,  $t_1 = D_1/n$  approximately. The loss of leak for the time  $t_1$  is therefore  $D_1^2A/2n$ . Therefore, when the leak is calculated for a given time  $t_2$ , the value obtained is less than the correct value, the

difference being equal to  $\frac{D_1^2 A}{2n} \frac{t_2}{t_1}$ , that is  $AD_1 t_2/2$ . Since

 $D_1$  and  $t_2$  are taken the same in all the measurements, and A is a constant, the difference between the correct leak and the calculated leak is the same in each case. Consequently, when the calculated leak obtained when no radiator is used is subtracted from the calculated leak obtained when a radiator is used, the correct value of M unaffected by leakage is obtained. This method of eliminating the loss of leak was especially advantageous in these experiments since the loss of leak could not have been easily obtained directly, and it could not be neglected since its magnitude was not negligible in comparison with that of the leak.

A set of measurements will now be described. A screen of some substance was placed in position, and the secondary radiation from a set of substances in terms of that from a standard substance determined. The screen was then replaced by one of different material, and the whole process

repeated, and so on. The measurements for determining the radiation from a substance in terms of that from a standard substance were carried out in the following manner:-Two readings were taken without any radiator. Two readings were then taken with the radiator under investigation placed in position. Lastly, two readings were taken with the standard radiator. This process was repeated at least seven or eight times. The mean of the first set of readings was then substracted from each mean of the two other sets of readings, the result giving the relative secondary radiation from the substance under investigation and the standard radiator.

The following numbers will give an idea of the relative magnitude of the leaks measured. A deflexion of 1800 scale-divisions in 4 minutes was obtained when the screen was of iron and '6 cm. thick, and no radiator was used. Deflexions of the same amount were obtained with a lead radiator 1.8 mm. thick in 3 minutes, and with a zinc radiator 3 mm. thick in 2 minutes 8 seconds. An electrometer of the Dolezalek type, fitted up with a telescope and scale, was used in these experiments. Since the leaks were all very small the experiments were very tedious, the determination of the amount of secondary radiation from a substance in terms of that from a standard substance requiring about three hours.

Table I. contains the results of some measurements carried out in the manner described. The first vertical column gives the nature of the radiators and their thickness. horizontal column gives the nature and thickness of the screens used. The numbers in each vertical column give the relative amounts of secondary radiation from the substances given in the first column, when the screen given at the top of the column was used. The radiation from lead. the standard substance, has been put equal to 100 for each The relative radiations obtained with the same screen depend, it will be observed, on the selective partial absorption of the radiations by the screen, and the nature of the secondary radiation emitted by each substance, and on the relative masses of the substances used. Since some of the radiation generated in a substance is absorbed by the substance, the nature of the radiation emitted by a given mass of substance must depend somewhat on its shape and size. The shape of each radiator was therefore made the same as that of the standard substance with which it was compared. The radiation from mercury was compared with that from lead by placing a quantity of mercury in a thin

celluloid dish 14 cm. long and 11 cm. broad, and comparing the radiation from the mercury with that from a lead plate having the same length and breadth as the dish. The depth of the mercury in the dish was 10 mm. and the thickness of the lead plate was 6 mm. In these measurements the screens were placed in a horizontal position underneath the ionization-chamber, and the mercury dish or lead plate placed in a horizontal position underneath the screen. The radiation

TABLE T.

Radiator and its thickness	Pb. 1·8 mm.	Zn. 6·5 mm.	Fe. 6·5 mm.	S. 9 mm.	Al. 7·5 mm.	C. 20 mm.	Card- board. 4 mm.
Pb	100	100	100	100	100	100	100
Hg	64.1	64.1	67.6	68.5	67.0	67:6	64.1
Zn 3 mm	156	268	253	225	214	186	186
Cu 3 "	183	330	303	278	257	233	223
Fe 3 "	172	311	304	264	244	214	230
S 2 ,,	150	260	249		223	186	187
Al 7.5 ,,	151	267	273	239		209	208
C 20 mm	167	343	377	347	334	274	284

TABLE II.

Radiator.	Pb.	Zn.	Fe.	S.	Al.	C.	Card- board.
Pb	64.1	37.3	39.5	44.4	46.7	53.7	53.8
Hg	41.1	23.9	26.7	30.4	31.3	36.3	34.2
Zn	100	190	100	100	100	100	100
Cu	117	123	120	122	120	125	120
Fe	110	116	120	117	114	115	127
S	96.3	97	98.4		104	99.8	101
Al	96.8	99.6	108	106		112	112
C	107.2	128	140	154	156:2	147	153

from the lead plate was taken equal to 100. The radiation from each of the other radiators was compared with that from a lead plate 1.8 mm. thick, and of the same length and breadth as these radiators, each of which was 28 cm. long and 24 cm. broad. The radiation from lead was taken, as before, equal to 100.

Table II. gives the same observations as Table I. except

that the value of the radiation from zinc has been put equal to 100 for each screen, and the values of the radiations from

the other substances changed correspondingly.

It will be seen from Table I. that when Pb is put equal to 100, the values of the radiation from Pb with the different screens (given in the horizontal column containing Hg) become approximately equal to one another. From Table II. it will be seen that when zinc is put equal to 100, the values of the radiations (with the different screens) from each of the substances Al, S, Fe, Cu, Zn, become approximately equal to one another. But the values of the radiations from C do not become equal to one another in either case. Thus the substances appear to fall roughly into three groups. The interpretation of this is that each member of a group radiates approximately the same kind of secondary rays, but the radiation from a group is as a whole different from that from some other group. Thus, if each of the substances of a group radiates the same kind of rays, a screen will diminish the radiation in the same proportion in each case whatever the selective absorbing nature of the screen. The relative radiations will therefore not be altered by a screen, and therefore when the radiations with the different screens from one of the substances of the group is put equal to 100, the values of the radiations from each of the other substances of the group will become approximately equal to one another. These considerations also show that the substances which do not belong to a group radiate rays which differ as a whole from the rays radiated by the group.

For convenience of reference we will denote by Group I. the substances Pb and Hg, including the substances which radiate the same kind of rays as Pb or Hg, if any exist. Similarly we will denote by Group II. the substances which radiate the same kind of rays as Zn, Cu, Fe, S, and Al; and by Group III. the substances which radiate the same kind

of rays as C.

The problem that presented itself next was to determine if there is any relation between the rays from the various groups of substances. This was done by the following method. The radiations from two substances A and B belonging to two different groups were compared—when the screen used was thin, and when it was much thicker. Now, if one of the substances, say A, radiates more rays which are well absorbed by the screen, than the other substance B, the ratio of radiation from A to that from B will decrease when the thickness of the screen is increased. In that case, we can

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say that the substance A at least radiates rays which are well absorbed by the substance of the screen. In this manner, substances belonging to different groups were compared with one another, using successively screens belonging to different groups. It was found that when there is an indication that a radiator radiates more rays which are well absorbed by the screen, than some other radiator, the effect may be made more pronounced by increasing the thickness of either radiator or of both. The reason for this will appear when the results of this investigation are discussed. It is obvious that the effect can also be increased by increasing the ratio of the thick screen to the thin one. For our present purpose it is only necessary to make sure that there is a change in

the ratios with increase of thickness of screen.

Table III. gives the results of some experiments carried out in the manner described. Let us first consider the results obtained when the substance of the screen used belonged to Group I. The first and third vertical columns of this part of the table give the radiators and their thicknesses. The column on the right of each of these columns gives the values of the secondary radiations corresponding to two different thicknesses of the screen, the nature of the screen being given at the top of the column. The radiation from lead has in each case been put equal to 100. It will be seen that there is a decrease in the ratio of the radiation from zinc to that from lead with an increase of thickness of the lead screen. Thus zinc radiates a greater proportion of rays which are well absorbed by lead than lead itself. reason for this, as will afterwards be seen, is that the rays generated in a radiating plate, of the kind best absorbed by the plate, are almost entirely absorbed by the plate. Further, since the substances which we have denoted by Group II. of which zinc is one, radiate approximately the same kind of rays, and the substances of Group I., of which lead is one, also radiate the same kind of rays, it follows that the substances of Group II. radiate a greater proportion of rays well absorbed by lead than the substances of Group I. If the substances of a group resemble one another in their absorption properties, this would be true for all the substances of Group I. besides lead. It will presently be shown in this connexion that the substances of Group II. possess the same absorption properties, and we may therefore take it for granted that this is true for all groups. Moreover, it will be seen, when the primary and secondary rays are compared, that the substances of each group possess the same absorption properties for the primary rays.

				i	
Radiator and its	Pb sc	ereen.	Radiator and its	Pb s	creen.
thickness.	1 mm.	4 mm.	thickness.	1 mm.	4 mm.
Pb 1.8 mm	100	100	Pb 1.8 mm	100	100
Zn 3 "	198	141	C 20 ,,	240	178
\$	Screens	belongi	ng to Group	II.	
Radiator and its	Fe so	ereen.	Radiator and its	Fe se	creen.
thickness.	1.3 mm.	4·3 mm.	thickness.	1·3 mm.	4·3 mm
Pb 1.8 mm	100	100	Zn 6.5 mm	100	100
<b>Z</b> n 6·5 ,,	252	290	C 20 ,,	355	329
	Al sc	reen.		Cu s	creen.
	3.8 mm.	7·5 mm.		1.6 mm.	4.6 mm
Pb 1.8 mm	100	100	Pb 1.8 mm	100	100
Zn 3 "	190	224	Zn 6·5 ,,	329	355
	Screen b	elongin	g to Group I	II.	
		elongin	g to Group I		ereen.
Radiator			Radiator		
Radiator and its	C sc	reen.	Radiator and its	C so	
Radiator and its thickness.	C sc	reen.	Radiator and its thickness.	4 mm.	24 mm
Radiator and its thickness.	4 mm.	24 mm. 100 237	Radiator and its thickness.	4 mm.	24 mm.
Radiator and its thickness.	4 mm. 100 230	24 mm. 100 237	Radiator and its thickness.	4 mm.	24 mm
Radiator and its thickness.	4 mm. 100 230 C ser	24 mm. 100 237	Radiator and its thickness.	4 mm.	24 mm.

It will be further seen in the table that the ratio of the radiation from lead to that from carbon is also increased with an increase of the thickness of the lead screen. Thus carbon radiates a greater proportion of rays which are well absorbed by lead than lead itself. It follows, therefore, reasoning in the same manner as before, that the substances of Group III. also radiate a greater proportion of rays which are well absorbed by a substance of Group I., than the

substances of Group I. themselves.

Let us next consider the results obtained when the substance of the screen used belonged to Group II. (The values for lead and zinc are put equal to 100 in each case.) It will be seen that the ratio of the radiation from lead to that from zinc is decreased with an increase in the thickness of the iron screen. Thus lead, a substance of Group I., radiates a greater proportion of rays well absorbed by iron, than zinc, a substance of Group II. It follows, therefore, that the substances of Group I. radiate a greater proportion of rays well absorbed by iron, a substance of Group II., than the substances of Group II. This was proved by experiment to be true for some other substances of Group II. besides iron. Thus, it was found (see table) that there is a decrease in the ratio of the radiation from lead to that from zinc, substances of Group I. and II., with an increase in the thickness of a screen of copper or aluminium, substances of Group II. From this it follows that the foregoing result is also true for aluminium and copper, and it may therefore be taken to be true for all the substances of Group II.

Further, the ratio of the radiation from carbon to that from zinc is decreased, as will be seen in the table, with an increase in the thickness of an iron screen. It follows, therefore, that the substances of Group III. also radiate a greater proportion of rays well absorbed by a substance of Group II., than the substances of Group II. themselves.

It remains to consider the results obtained when the substance of the screen used belonged to Group III. (The values for lead and zinc are put equal to 100 in each case.) It will be seen that the ratio of the radiation from lead (a substance of Group I.) to the radiation from carbon (a substance of Group III.) is decreased with an increase in the thickness of the carbon screen. The decrease, it will be observed, is greater for the thicker of the two lead radiators used. Further, the ratio of the radiation from zinc (a substance of Group II.) to the radiation from carbon, is also decreased with an increase of the thickness of the carbon screen. It follows, therefore, in the same manner as before,

that the substances of both Group I. and Group II. radiate a greater proportion of rays which are well absorbed by a substance of Group III., than the substances of Group III. themselves.

Thus we have the general result that the substances of any two groups radiate a greater proportion of rays which are well absorbed by the substances of the remaining group, than the substances of this group radiate themselves. It will now be shown that it follows from this result that each group of substances radiates two groups of rays, each of which is best absorbed by one of the remaining groups of substances. Let us begin with considering the radiation from the substances of Group I. We are given that Group I. and Group II. radiate a greater proportion of rays which are well absorbed by Group III., than Group III. itself; and also that Group I. and Group III. radiate a greater proportion of rays which are well absorbed by Group II., than Group II. Hence Group I. radiates rays which are well absorbed by Group III., and rays which are well absorbed by Group II. These two groups of rays are different, since the former group is radiated in a greater proportion by Group II. than by Group III., and the latter group is radiated in a greater proportion by Group III. than by Group II. In a similar manner, the above statement may be proved for the other

groups of substances.

Thus the substances of Group I. radiate two groups of rays, one of which is best absorbed by the substances of Group II. and the other best absorbed by the substances of Group III., and the substances of Group II. radiate two groups of rays, one of which is best absorbed by the substances of Group III. and the other best absorbed by the substances of Group I. It follows from this that the substances of Groups I. and II. radiate one group of rays in common, the group being best absorbed by the substances of Group III. In the same manner it can be shown that any other pair of groups of substances radiate a group of rays in common. Since there are three groups of substances, each of which radiates two groups of rays, there are at least three different groups of secondary y rays. But since the substances in Tables I. and II. fall approximately only into three groups, it follows that the rays of a group consist of different kinds of rays, but which differ less from one another than from the rays radiated by some other group. We will return to this point about the grouping of the rays later on. It will be convenient to distinguish these groups of rays from one another by names. Thus the secondary rays which

are best absorbed by the substances of Group I. will be called Group I. rays, and a similar name given to each of the other groups of rays corresponding to the group of substances by which the rays are best absorbed. According to this notation the substances of Group I. radiate secondary

rays of Group II. and Group III., and so on.

We have seen (Table III.) that the increase in the ratio of the radiations from two substances with an increase of thickness of screen, becomes more marked when the thickness of one of the radiators (or of both) is increased. This is due to secondary rays of all three groups being generated in a substance, but one of the groups being more easily absorbed by the substance than either of the other groups. The radiation from a substance would then consist principally of two groups of rays, and a small proportion of rays of the remaining group; and the difference in the nature of the radiations from two substances would therefore become more marked the greater their thickness.

The changes observed in the ratios of the radiations with the thickness of screen are small, but they can be accurately measured. The reason for their smallness will now be apparent from the deductions made from the results. Since two substances of two different groups radiate (at least) one group of rays in common, this group of rays will mask to some extent the relative change in the radiations produced by an increase of the thickness of the screen. Moreover, the fact that all the groups of rays are absorbed more or less by a substance will also have the effect of making the change

small.

It will be profitable now to compare the results so far obtained with the result quoted in the beginning of this paper from a previous paper, namely, that the primary  $\gamma$  rays of radium consist in part of three groups of rays. In the paper mentioned it was shown that one of the groups of rays is best absorbed by lead, mercury, and bismuth, and one group best absorbed by tin, zinc, copper, nickel, iron, sulphur, and aluminium, and the remaining group best absorbed by carbon. It will be seen that each of these three groups of substances defined in this paper. It appears, therefore, that the primary  $\dot{\gamma}$  rays of radium consist of at least three groups which possess the same property of selective absorption as the three groups of secondary rays discussed in this paper.

It became of interest next to investigate if the secondary  $\gamma$  rays possess the same penetrating power as the primary rays. The measurements for determining the coefficients of

absorption of the secondary rays from different substances were carried out in the following manner:-Readings were taken, using no radiator, with a thin screen of the substance whose coefficient of absorption was to be found placed at C (see fig. 1), and then with a thicker screen of the same substance in place of the thin one. The radiator, which was 28 cm. long and 12 cm. broad in each case, was then placed at B, and the readings repeated. Each of the readings taken without the radiator was then subtracted from the corresponding reading taken with the radiator, the result giving the relative radiations corresponding to the two different thicknesses of the screen. The radiating plate was made as small as was possible without reducing the leak to an inconveniently small quantity. This was done in order that the maximum angle which the secondary rays made with the normal to the screen might be as small as possible, in the actual case the angle was about  $45^{\circ}$ . If  $\lambda$  denote the coefficient of absorption, we have then  $I_1 = I_0 e^{-x_1\lambda}$ , and  $I_2 = I_0 e^{-x_2\lambda}$ , where  $I_1$  is the leak in the chamber when the thickness of the screen is  $x_1$ , and  $I_2$  the leak when the thickness of the screen is  $x_2$ , and  $I_0$  the leak that would be obtained without a screen. The elimination of I<sub>0</sub> gives an equation from which  $\lambda$  is obtained. The value of the coefficient of absorption is somewhat influenced by the fact that the secondary rays traversed the screen at various angles. But it was found on calculation that this did not introduce any very appreciable error. Since the nature of the radiation from a substance depends to some extent on its thickness, the coefficient of absorption depends to some extent on the thickness of the radiator. Thus, in the case of a very thin radiator, the radiation would consist of the three groups of rays in almost equal amount; but as the thickness of the radiator is increased, the proportion of one of the groups is much decreased on account of being more easily absorbed by the plate than the other groups. It was on account of these considerations that the coefficient of absorption was not determined with greater accuracy than that given by two different thicknesses of the screen.

Table IV. gives the results obtained with the secondary rays from the radiators lead, zinc, and carbon, each of which belongs to one of the three groups of substances defined in this paper. The first column contains the substances whose coefficients of absorption were found. The coefficients of absorption of a substance corresponding to the different secondary rays radiated by the substances given in the first horizontal row, are given in the same horizontal row which

TABLE IV.

Absorbing substance.	Secondary rays from Zn (of Group II.).	Secondary rays from Pb (of Group I.).	Secondary rays from C (of Group III.)	Primary rays.
Pb (Group I.)	λ=4.84	λ=1.85	λ=7.5	λ=.77
Fe )	λ=:365	λ=:628	λ=2:72	λ=:28
Cu (Group II.).	$\lambda = .794$	λ=.894	******	λ=·31
$ \mathbf{z}_{\mathrm{n}} $	λ= 69		•••••	$\lambda = 28$
C (Group III.)	•••••	• • • • • • •	λ=:049	

contains the substance. It will be seen that on the whole the coefficients of absorption of the secondary rays are much greater than those of the primary rays. The secondary rays we are dealing with, it will be observed, consist in each case of at least two different groups. Thus it follows that the three groups of primary rays of radium with which we are dealing in this paper are transformed by a substance into three groups of secondary rays, which possess the same property of selective absorption as the primary rays, but which are, on the whole, softer or more easily absorbed than the primary rays. This result shows that we must distinguish between selective absorption and softness of  $\gamma$  rays. distinction is best illustrated as follows:—Suppose we were able to isolate a group of primary y rays, and then measure its absorption by three different substances, each of which belongs to one of the groups defined in this paper. We would then find that each of the substances absorbs the group of rays to some extent, but one substance to a greater extent than either of the remaining two substances. In the case of the corresponding group of secondary rays, we would find that each of the substances absorbs the group of rays to a greater extent than the primary group, and that the same substance as before absorbs to a greater extent the group than either of the remaining two substances.

It may be pointed out that the results contained in Table IV. bear out some of the conclusions drawn from the results in Table III. Thus, the secondary radiation from lead, a substance of Group I., is better absorbed by iron and copper, substances of Group II., than the secondary radiation from zinc, a substance of the latter group. Also, the secondary radiation from carbon, a substance of Group III.,

is better absorbed by iron, a substance of Group II., than the radiation from zinc, a substance of the latter group, and so on. This shows, as before, that the substances of a group radiate those rays in least amount which they best absorb. It should be observed that we can only compare the coefficients of absorption for the same substance.

We have seen that the three groups of primary rays possess the same properties of selective absorption as the three groups of secondary rays. But it will be observed that it does not follow from this that a primary group of rays gives rise to the corresponding group of secondary rays, although this is very probable. Some further experiments were therefore made to demonstrate this. The experiments were carried out in the following manner. The coefficient of absorption of the secondary rays from a substance of one of the groups—say Group III.—was determined for a substance belonging to a different group—say Group II. A thick screen of a substance belonging to Group II. was then placed over the radium and the coefficient of absorption again determined; the secondary rays being now produced by the primary rays which penetrated the thick screen placed over the radium. Now, since the radiator belongs to Group III., it radiates rays of Group II. and Group I.; and since the substance whose coefficient of absorption is measured belongs to Group II., the part of the secondary radiation belonging to Group II. is absorbed to a greater extent by the substance than the remaining part. Therefore, if the secondary rays of Group II. are produced by the primary rays of Group II., the coefficient of absorption should decrease when the primary rays are passed through a screen of a substance of Group II. In the same manner, obviously, it may be investigated whether there is a relation between the primary and secondary group for other groups of rays. magnitude of the decrease of the coefficient of absorption will be influenced by a large number of things. Thus it depends on the relative strength of the group of primary rays under investigation to that of the remaining groups. It also depends on the extent the screen over the radium absorbs the other groups besides the one which is best absorbed, and

In Table V. some experimental results are given. The substances whose coefficient of absorption was determined under the different conditions, are given in the first vertical column, and their coefficients of absorption in adjacent horizontal columns. The horizontal column above the column containing the coefficients of absorption for a substance gives

the conditions under which each coefficient was determined. It will be seen that the coefficient of absorption of each substance is decreased with a screen of the same substance placed over the radium. The results, therefore, show that the primary rays of Group I. and Group II. are transformed into corresponding groups of secondary rays. We may take it for granted, therefore, that this is the case with each primary group of rays.

Since the secondary  $\gamma$  rays consist of at least three groups, and, as we have just seen, a group of secondary rays is caused by the transformation of a primary group possessing similar properties, it follows that the primary rays of radium consist of at least three groups, each of which is selectively absorbed by one of three groups of substances. We have thus established in an entirely different manner a result

obtained in a previous paper.

Since the substances in Tables I. and II. fall approximately only into groups, the grouping of part of the primary and secondary radiation into three groups is therefore only a rough one. It appears very probable, therefore, that there are other primary and secondary rays which are not included in any one of these groups. Some of these rays or groups of rays would become apparent by investigating the secondary radiation from other substances than those dealt with in this

paper. It may be pointed out in this connexion that the selective absorption properties of the elements probably do not change gradually with the atomic weight. Thus, aluminium and zinc possess approximately the same property of selective absorption, while that of carbon is different, though the ratio of the atomic weight of zinc to that of aluminium is about the same as the ratio of the atomic weight of aluminium to that of carbon. It will be observed that the existence of other rays or groups of rays than those dealt with in this paper, does not invalidate any of the deductions made. The existence of other rays or groups of rays when two groups of rays are compared, has the effect of making the properties of the latter appear less marked. Thus, it is evident that the larger the number of different kinds of rays in a beam of rays, the smaller will be the decrease in the strength of the beam when a screen which absorbs best one kind of rays is placed in the path of the beam. This indicates some measurements from which a rough indication of the distribution of the γ rays amongst the different kinds of rays may be obtained, and which will now be described. The amount of secondary radiation from a zinc plate which penetrated a plate of lead 1.8 mm. thick was found to be equal to 795, in arbitrary units; and the amount which penetrated a zinc plate 3 mm. thick (of about the same mass as the lead plate) was found to be equal to 2258. Let the total radiation from the zinc plate be denoted by (A+B), where A denotes the radiation of Group I. and B denotes the remaining radiation. Suppose that the lead plate (a substance of Group I.) allows the fraction u of the radiation A to penetrate the plate. Since the lead and zinc plates are approximately of equal mass, we may suppose as a first approximation that the same fraction w of the radiation B penetrates each plate, where w, it will be observed, must be larger than u. The amount of radiation measured when the zinc and lead plates were successively used as screen was therefore (wA + wB) and (uA + wB) respectively, and therefore in this experiment

$$uA + wB = 795$$
 and  $wA + uB = 2258$ .

From these two equations we have

$$wA - uA = 1463,$$

and therefore

$$\frac{wA - uA}{wB + uA} = \frac{1463}{795}.$$

Now, if u=0, that is, if all the radiation of Group I. is absorbed by the lead plate, the right-hand side of the last equation gives the ratio of the radiation of Group I. to the

remaining radiation. If only part of the radiation of Group I. is absorbed, as is actually the case, the ratio A/B is greater than this value. For it will be easily seen that if u is increased and A kept constant, B must decrease in order that the value of the right-hand side of the equation may remain the same. The value of B on the above assumption is therefore smaller than that of A. There is therefore little room for the radiation B to consist of a number of groups of rays of the same intensity as A, or the secondary rays from zinc to consist of a number of groups (of intensity A) much greater than two. It seems therefore that a large part of the primary and secondary radiation is represented in each case by the three

groups of rays defined in this paper.

The relative total amount of y radiation produced per unit mass in a substance, a quantity which will now be discussed, cannot be obtained, since each radiating substance absorbs to a large extent one of the groups of rays generated in the substance. Moreover, the proportion of  $\gamma$  rays absorbed by the screen which is used to cut off the  $\beta$  rays, is not the same with each radiating substance but depends on the nature of the substance. But since the substances belonging to any one of the groups defined in this paper radiate the same two groups of rays, the values of the radiations obtained for a group of substances give the relative amounts of radiation of these two groups of rays produced per c.c., if the proportion of this radiation absorbed by the radiator is the same with each. It will be seen that in this case the screen absorbs the same proportion of the radiation from each substance, and therefore does not alter the values of the radiations relatively. Table VI. gives the

TABLE VI.

Radiator.	Mass of radiator.	Radiation from radiator.	Radiation per unit mass.
Pb	$1652~\mathrm{gms}.$	53.8	52:7
Zn	1622 gms.	100	100
Cu	1890 "	121	103.7
Fe	1818 "	117	104.3
S	1305 "	99.3	123-3
A1	1455 "	105.7	117.6
C	2076 gms.	153	119.4

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relative amounts of radiation of a number of substances. The first two columns in the table give the nature and mass of the radiator, and the third column gives the values of the secondary radiation. The fourth column gives the radiation per unit mass calculated on the assumption that the amount of radiation absorbed by each radiator is proportional to its mass. The values for carbon and lead are those obtained with the cardboard screen, while the values for the substances of Group II. are the mean of the values given in Table II.; they differ little from those obtained with the cardboard screen. The values of the radiation per c.c. of the substances of Group II. only in the table can be compared with one another, as just explained. They give approximately the relative amounts of radiation of Groups II. and III. produced per c.c. in each substance. It will be seen that the values do not differ much from one another. This is a result that would be expected if the mass of an atom is proportional to the number of electrons it contains. The values obtained would probably be more nearly equal to one another if the masses of the radiators used had been equal to one another. The difference in the calculated amount of radiation per unit mass for lead and a substance of Group II. cannot be altogether due to the selective absorption of the cardboard screen, or to a difference in the absorption of the radiated It seems to indicate, therefore, that the radiation of Groups II. and III. produced in a unit mass of lead is less than the radiation of Groups I. and III. produced in unit mass of a substance of Group II. This is probably due to the amount of radiation of Group I. being greater than that of either Group II. or Group III. We obtained some evidence of this, it will be remembered, when discussing the number of different primary and secondary groups of rays.

We will now discuss at some length the transformation of primary rays into secondary. When a beam of primary  $\gamma$  rays passes through a plate, it generates secondary rays in the plate corresponding to the different groups of primary rays; the amount of radiation in a secondary group of rays depending on the absorption of the corresponding primary group. Since one of the primary groups of rays will be better absorbed by the plate than either of the remaining groups, the amount of secondary radiation generated corresponding to this group must be larger than that corresponding to either of the remaining groups. The amount and nature of the secondary radiation which is not absorbed by the plate, and which is therefore radiated away from the plate, depends on the selective absorption of the different groups of rays by

the plate. And since the primary and secondary rays possess the same properties of selective absorption, that group of secondary rays is best absorbed which corresponds to the best absorbed group of primary rays. Thus the group of secondary rays which is produced in a larger amount in a plate than the other groups, is best absorbed by the plate. Now, the experiments described in this paper show that the amount of secondary radiation from a thick plate corresponding to the group of primary y rays which is best absorbed, is small in comparison with the secondary rays corresponding to either of the other groups of primary rays. If the amount of secondary rays produced is proportional to the absorption of the primary rays, and the proportion absorbed of each group of secondary rays by the plate is the same multiple of the proportion absorbed by the plate of the corresponding group of primary rays, this would obviously not be the case. Let us therefore investigate this more closely. We will make the following assumptions and compare the conclusions that can be drawn from them with the results of experiment. Suppose that the coefficient of absorption of a group of secondary rays generated in a substance is for a distance dx in that substance n times that of the primary rays, and the coefficient of absorption of the tertiary rays n times that of the secondary, and so on. Suppose also that the fraction m of the energy absorbed of the primary rays in a distance dx is converted into secondary radiation, and the same fraction of the energy absorbed of the secondary radiation converted into tertiary radiation, and so on. Let us further suppose that n and m are the same for all substances. It will now be shown that on these assumptions the amount of secondary radiation from a plate corresponding to the group of primary rays which is best absorbed, would be greater than that corresponding to any other primary group. Let us consider the secondary radiation produced by two primary groups of rays which we will denote by A and B, where the group A is better absorbed than the group B. The amount of radiation from a given plate will not be altered if it be compressed to a less thickness, for the amount of radiation produced depends on the number of absorbing and radiating molecules only, and not on their distance of separation. Suppose then that a plate is compressed to such a thickness that the coefficient of absorption of the rays of group B (for a distance dx) is the same as that of the rays of group A in an uncompressed plate. Then it follows that the coefficients of absorption of the secondary rays, and rays of higher order, corresponding to group B in the compressed

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plate, are the same as the coefficients of absorption of the secondary and higher rays corresponding to group A in the uncompressed plate. The value of m, it will be observed. will not be altered by the compression. Therefore the amount of secondary radiation corresponding to group B radiated by the compressed plate is equal to the amount of secondary radiation corresponding to group A radiated by an uncompressed plate of the same thickness and area. The amount of secondary radiation of group B from an uncompressed plate must therefore be smaller than the amount of secondary radiation of group A from the same plate; that is, the amount of secondary radiation corresponding to the more absorbable primary group of rays is greater than that corresponding to the other less absorbable group. But this result is exactly opposite to that obtained by experiment. Let us see what this means. According to the foregoing, the amount of secondary radiation generated by a group of primary rays in an element of volume of a substance is proportional to  $m\lambda$ , where  $\lambda$  is the coefficient of absorption of the rays. The amount of secondary radiation which is not absorbed by the element of volume, and which is therefore radiated away from the element, is approximately proportional to

$$(m\lambda - (m\lambda)n\lambda)$$
, or  $m\lambda^2 \left(\frac{1}{\lambda} - n\right)$ .

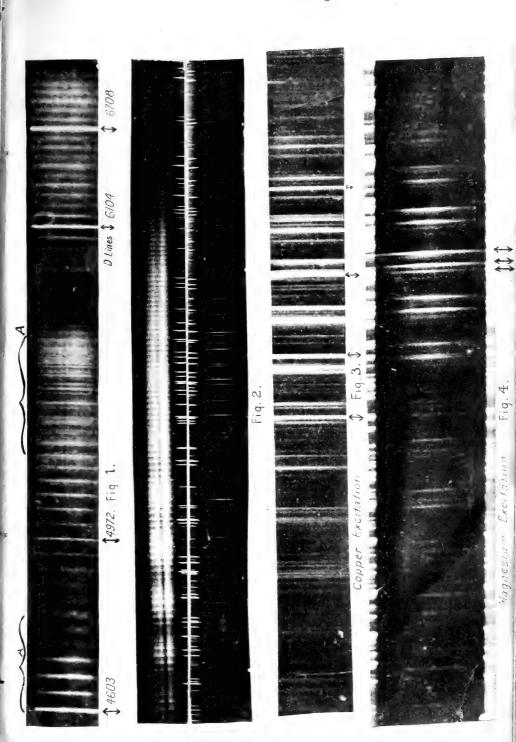
Since  $\lambda^2$  increases more rapidly with an increase of  $\lambda$  than  $\left(\frac{1}{\lambda}-n\right)$  decreases,  $m\lambda^2\left(\frac{1}{\lambda}-n\right)$  increases with an increase of  $\lambda$ , and we obtain as before that the amount of secondary radiation increases with the absorption of the primary rays. It follows, therefore, from the experiments that m and n cannot be the same for each group of primary rays. And since  $m^2\left(\frac{1}{\lambda}-n\right)$  must decrease with  $\lambda$ , either m must decrease

or n increase with  $\lambda$ , or both vary in this way with  $\lambda$ . It seems improbable though that the decrease of the amount of secondary radiation with increase of absorption of the primary group is due to a decrease of m; that is, to a decrease of the fraction of the absorbed energy which is converted into secondary rays. It is more probably due to an increase of n, that is, an increase in the relative absorption of a secondary group to a primary group with increase of absorption of the primary group. This may also be expressed by saying that the selective absorption is more marked for the secondary rays than for the primary. If the transformation of primary rays into secondary is a

resonance effect, we would expect that the absorption of the secondary rays would be, on the whole, greater than that of the primary, and that the selective absorption of the secondary rays would be more marked than that of the primary. It becomes of interest, therefore, to investigate what the results of these experiments indicate on the æther-pulse theory of the

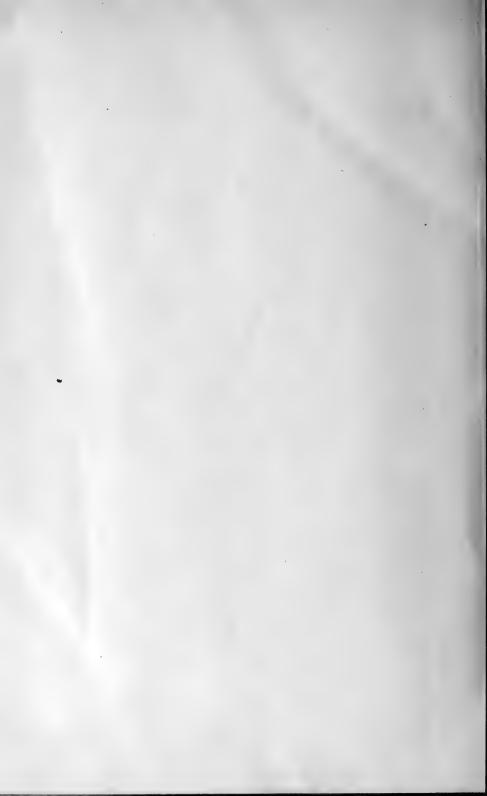
y rays.

According to this theory, one æther pulse may differ from another in three different ways, namely—thickness of pulse; magnitude of the electric force at, say, midway between the edges of the pulse; and the function which expresses the relation between the ratio of the force at any point in the pulse to that midway between the edges of the pulse and the distance of the point from one of the edges of the pulse. This function will be called throughout the paper the forcerelation of the pulse. It follows also from the theory that the force-relation of a pulse and its breadth remain unchanged as the distance of the pulse from the source increases, but the force in the pulse is everywhere decreased. The selective absorption of some members of a number of different æther pulses must now be explained by differences between the pulses in the magnitude of one of the properties of an æther pulse. It was observed in these experiments that the selective absorption of the y rays is independent of the distance of the rays from their source. It follows, therefore, that selective absorption cannot be due to the different groups of rays differing from one another in the magnitude of the force in the pulse, for, if selective absorption were due to this, a group of y rays at a given distance would possess the same properties as some other group at some other distance. It is also improbable that it is due to the groups of rays differing from one another in the breadth of the æther pulse. For there would be nothing in this case to distinguish a broad pulse from a narrow one, as far as the absorbing electrons are concerned, till both had passed completely over the electrons. One would expect then that an electron which absorbs a pulse of certain breadth well, would absorb to a greater or less extent other pulses also. It is difficult to see, therefore, if selective absorption is entirely due to differences in breadth of pulse, why a narrow pulse is better absorbed than a broad one by one substance, while the opposite is the case with some other substance. We conclude, therefore, that selective absorption is probably due to the existence of groups of rays which differ from one another in the force-relations of their pulses. Since the secondary rays possess the same properties of selective absorption as the primary, the form of the force-









relation is not altered when a group of primary rays is

transformed into a group of secondary rays.

The difference in the absorption of a primary and secondary pulse (which, as we have seen, must be distinguished from selective absorption) is probably due in part or on the whole to the form of the force-relation of the secondary pulse satisfying the condition for absorption better than the primary pulse. But there is probably some other cause operating besides this one. Now, since the coefficient of absorption of a  $\gamma$  pulse is independent of the distance from its source, the difference in the absorption cannot be due to a difference in the force of the pulse. The difference in the absorption is therefore probably due in part to a difference in the breadth of the pulse, the pulses in a group of secondary rays being probably broader than those in the corresponding group of

primary rays.

The production of secondary rays and their properties may then be explained on general lines as follows. Each electron in an atom is in equilibrium under the action of the forces in the atom, and when displaced from its position of equilibrium by the force in a pulse passing over it, the atomic forces tend to bring it back to its previous position. The maximum absorption of energy from the pulse by the electron will take place if the force acting on the electron due to the electric force in the pulse is always proportional to the force of restitution of the electron, whether both forces act in the same or in opposite directions. This is the condition, it will be observed, that acceleration of motion of the electron must take place all the time the pulse is acting upon it. That this condition may be satisfied depends on the form of the force-relation of the pulse as well as its breadth. The form of the forcerelation of a pulse and its breadth, it may be pointed out in passing, may easily be such that at the instant the electron ceases to be under the influence of the pulse after having been deflected, it is at rest in its position of equilibrium. a pulse passes over an electron which does not exactly satisfy the conditions for best absorption (we may suppose the pulse narrower for one thing than required by these conditions), the pulse radiated by the electron will satisfy these conditions much better, and will therefore be more easily absorbed by a similar electron than the primary pulse. If the pulse satisfies the conditions for best absorption to a small extent only, it will be only slightly absorbed, and the secondary pulse will not be so soft in comparison with the primary as in the foregoing case. The selective absorption of a group of primary y rays by a substance may then be explained by the force-Phil. Mag. S. 6. Vol. 15. No. 89. May 1908.

relation and breadth of pulse of the pulses of the group satisfying very approximately the conditions for best absorption for a number of electrons, while the other groups of rays do not satisfy these conditions and are therefore not absorbed by these electrons. But since the other groups of rays are also absorbed to some extent by the substance, the pulses satisfy to some extent the conditions for best absorption for some other electrons in the atom. The secondary rays produced in the substance under these conditions will then be on the whole softer than the primary rays, and possess the same properties of selective absorption as the primary rays, but in a more marked degree.

#### Conclusions.

It has been shown in this paper that the substances Pb. Hg, Zn, Cu, Fe, S, Al, and C, whose secondary radiation was measured, could be roughly divided into three groups. each group of substances radiating rays which differ as a whole from those radiated by the other groups. From this result and the results of other experiments described in the paper, it was deduced that a part of the primary y radiation from radium and the secondary radiation which it produces could be roughly divided into three groups. The rays of each of these groups are not homogeneous, but consist of different kinds of rays which may be said to differ less from one another than from the rays of some other group. It was shown that the three secondary groups of rays possess the same properties of selective absorption as the corresponding primary groups, but are on the whole more easily absorbed. Thus, one of the groups of primary rays is better absorbed than the other primary groups by the substances Pb and Hg. and one of the other primary groups is better absorbed than the other groups by C, and the remaining group of primary rays is better absorbed than the other groups by Zn, Cu, Fe, The three corresponding secondary groups S, and Al. possess the same property, except that each secondary group is softer or more easily absorbed than its corresponding primary group. There are probably other rays or groups of rays in a primary or secondary beam of rays besides those investigated in these experiments.

It was also found that a substance radiates those secondary rays in least amount which it best absorbs. This is due to the substance absorbing to a large extent that part of the radiation generated in the substance which is easily absorbed by the substance. The absorbed radiation—that is, the radiation which is not able to get out of the plate—is probably transformed into secondary cathode radiation and other forms of energy.

It is very probable that similar relations exist between primary and secondary X rays. The writer hopes to make some experiments in the near future to test this point.

In conclusion I wish to thank Prof. Thomson for his keen interest and ever ready advice during these experiments.

Cavendish Laboratory, February 18, 1908.

LX, An Experimental Investigation of the Nature of the  $\gamma$  Rays. By W. H. Bragg, M.A., F.R.S., Elder Professor of Mathematics and Physics in the University of Adelaide, and J. P. V. Madsen, D.Sc., Lecturer on Electrical Engineering \*.

In papers recently published in the Proceedings of the Royal Society of South Australia (May and June 1907) and in the Philosophical Magazine (October 1907) an attempt was made to show that the æther-pulse theory of  $\gamma$  and X rays might prove to be incorrect after all, and that most of the known properties of these rays could be explained more simply and directly on the supposition that they were material and consisted of neutral pairs. The arguments were based on a comparison of known phenomena with deductions from each of the two opposing hypotheses. At that time there did not seem to be any opportunity of appeal to a decisive experiment.

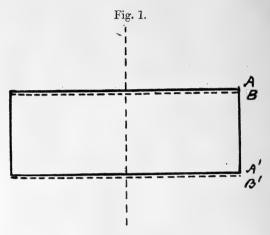
The object of this paper is to give a preliminary account of an investigation which appears to us to give the final answer as regards the  $\gamma$  rays, and to show that they are material in nature.

The argument is as follows:-

Secondary radiation which is excited in an atom by a passing wave or pulse must be distributed symmetrically with regard to a plane passing through the atom perpendicular to the direction of motion of the pulse. If we speak of the primary pulse as going forwards, the secondary radiation is just as likely to go backwards as forwards. This is a well-recognized principle. For example, J. J. Thomson divides the secondary radiation due to  $\gamma$  rays into two equal parts which he supposes to move away symmetrically in opposite directions, and, for convenience of calculation, parallel to the direction of the primary rays ('Conduction of

<sup>\*</sup> Communicated by the Physical Society: read April 10, 1908.

Electricity through Gases,' p. 406). Suppose, therefore, a pencil of  $\gamma$  rays to pass normally through a plate so thin that its absorption may be neglected, the secondary radiation should be exactly the same on the two sides of the plate in amount, in quality, and in distribution; and it ought not to be possible to discover, by any comparison of the secondary radiations on the two sides, which is the face of entry and which of emergence.



Consider now the ionization-chamber represented in fig. 1. The two ends are closed by plates, of which A and A' are alike; so also are B and B'. The material of A and A' is different to that of B and B'. The nature of the side walls is of no consequence. A pencil of  $\gamma$  rays passes along the axis of the chamber, which is represented by a dotted line. The ionization current within the chamber is measured as usual by inserting a high-potential electrode connected to an electroscope.

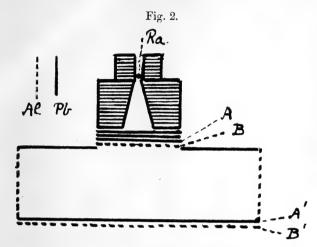
When the plates A and B are inverted there is a change in the amount of the current: so also when A' and B' are inverted. By an extension of the principle already stated it ought not to be possible, on the æther-pulse theory, to discover which way the rays are going (up or down in the figure) by comparing the consequence of inverting A and B

with that of inverting A' and B'.

As a matter of fact the direction can be discovered with ease; the more easily the greater the difference between the atomic weights of A and B.

For example, in one experiment of ours the chamber was of cylindrical form, 7.5 cms. high and 25 cms. diameter.

The plates used were aluminium and lead; the thickness of each plate was a little less than 2 mm. Inversion of the top plates A and B made a difference in favour of Al of less



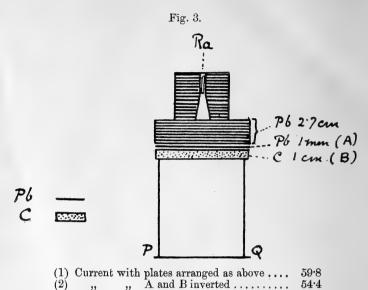
than 1 per cent.; i. e., the current was slightly larger when the Al was next the chamber. On the other hand, inversion of the bottom plates made a difference of 44 per cent. in favour of Pb; i.e., the current was 44 per cent. larger when the Pb was on top. The details are shown in the figure. Allowance was made for all radiation other than that which proceeded down the conical opening in the lead block.

It may be well to point out that this effect cannot be ascribed to any complication due to secondary or tertiary rays. No doubt the radiation in the chamber is very complex; but the fact is immaterial. Provided that the chamber is symmetrical in the first place, then the secondaries must be symmetrical also if the æther-pulse theory is correct, and therefore the tertiaries and so on. Nor is it necessary to consider whether the secondary radiations are  $\beta$  rays or scattered  $\gamma$  rays.

Also it must be remembered that the secondary radiations which enter the chamber have their origin almost entirely in a very few millimetres of material bordering on the chamber. Therefore the  $\gamma$  rays are in almost exactly the same condition, both as to quality and as to quantity, when they excite secondary radiations from the top plate as they enter the chamber, and secondary radiations from the bottom plate as they leave.

The details of the experiment may be varied greatly; but

in all the cases we have tried the want of symmetry is obvious. In fig. 3 are shown the details of one other case, in which



carbon and lead were the materials used, and the form of the chamber was different. It seems unnecessary to give more, because in the first place the experiments are easy to repeat; and in the second place, the complete quantitative analysis of the figures depends on several factors, the influence of which is imperfectly understood, such as the previous screening of the rays, the form of the chamber, and the respective parts played by the original  $\gamma$  rays, cathode rays, and secondary  $\gamma$  rays if any such exist. The experiments as they stand show how far away is that symmetry which the æther-pulse theory demands. It seems to us that there is no escape from the conclusion that the  $\gamma$  rays are not æther pulses.

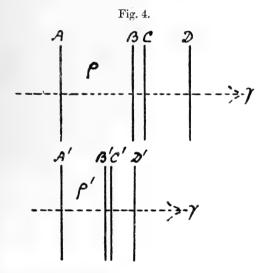
(3) As in (1), but base PQ changed to carbon.

Let us therefore proceed to consider the hypothesis that the  $\gamma$  rays are material. In the paper already mentioned it was argued that they might well consist of neutral pairs, liable to be broken up on encountering atoms or parts of atoms; and that the secondary cathode radiations might be the negative particles thus set free. Let us suppose, provisionally, that the particles when set free move at first in the direction of the  $\gamma$  stream, but are subsequently scattered in the usual manner of  $\beta$  rays. [It is here that the absence

of symmetry arises. On the pulse theory the particles should go equally backwards and forwards; indeed, if they were ejected by atomic explosions, the result of energy accumulated by passing pulses as suggested by J. J. Thomson in the case of X rays, they would move equally in all directions.

Wigger gives a table (Jahrbuch der Radioaktivität, Bd. ii. p. 431) showing that the  $\gamma$  rays are absorbed according to a density law pretty strictly, except for the smaller thicknesses in the case of the substances of larger atomic weight. Assume this law to hold good: and also assume for the present that the absorption of  $\beta$  rays follows the density law. The latter is only roughly true, of course; but we may deal with quantities in a broad fashion first, and make the proper amendments afterwards.

We can now compare the quantities of cathode radiation



which should emerge from the far sides of two plates of different densities,  $\rho$  and  $\rho'$ . Let these be represented by AD and A'D' in the figure; and let BC and B'C' be corresponding strata of equal weight, in fact let AB/A'B'=BC/B'C'=CD/C'D'= $\rho'/\rho$ . Let the plates be crossed by equal pencils of  $\gamma$  rays, as shown in the figure. A certain quantity of  $\gamma$  radiation is absorbed in crossing BC: in the language of our present hypothesis we should say that a certain number of  $\gamma$  particles are stripped of their positives, and the negative remainders go on. An equal number of

negatives are set free in B'C' because the two strata are of equal weight. Of those set free in BC only a certain number emerge from the face D because of the absorption of the plate CD. Since CD and C'D' are of equal weight a similar absorption occurs in the case of the particles set free in B'C'. Thus the same number emerges from each plate. Integrating for all effective strata, the whole cathode radia-

tions emerging from the two plates are equal.

We thus find that if the absorptions of  $\beta$  and  $\gamma$  rays both followed the density law, the secondary cathode radiation on the far side of a plate—we may call it the "emergence" radiation—would be the same for all materials. There should be no such relation between the amount of the radiation and the atomic weight of the plate as various observers have shown to be true for the secondary cathode radiation of "incidence," a relation which is closely parallel to that found in the case of  $\beta$  rays.

Experiment is in agreement with this theory, for it shows that no such relation exists in respect to the emergence radiations: in marked contrast to what happens in the case of the radiation from the front sides of the plates of various

materials—the incidence radiations.

It is true that the emergence radiations are not all equal, but this is to be expected, because (1) the amount of secondary cathode radiation depends, as Kleeman has shown, on the previous screening of the  $\gamma$  rays, (2) the  $\beta$  rays are not absorbed strictly according to a density law, (3) the y rays also depart from this law. We have made no serious attempt as yet to disentangle the effects of these various disturbing factors. In fact the task promises to be long and intricate, for it will be necessary to find out how much of the ionization in the chamber is due to each class of rays: to discover the law of distribution of the radiations in space so that the form of the chamber may be allowed for, if necessary: to find out the nature of the departures from the density law of those  $\beta$  and  $\gamma$  rays which are in question, and so on. theless the results are satisfactory, so far as we have gone. The amount of emergence radiation is found to depend on the previous screening of the rays. In one case the inversion of a C, Pb pair of plates from -> C, Pb to Pb, C altered the current in the ratio 1:1.11 when the rays had been previously screened by Pb; but in the ratio 1: 96 when the screen was changed to C. Again, when the rays had previously passed through an iron screen, current in the proportion 1:1.12, but when a lead screen was

substituted for an iron one the change was 1:1.04. In illustration of the effect of the second disturbing factor mentioned above, we have found that, other things being equal, the substances of small atomic weight give the most secondary radiation, in a general way; and it may be no coincidence that in some cases we have found Sn and Fe to give surprisingly small amounts. This is in agreement with what is to be expected; for it is clear, on consideration of the argument already given, that the greater the  $\beta$ -ray absorption of a substance in proportion to its density, the less "emergence" radiation should issue from it. Some observers have found Sn and Fe to possess exceptional absorbing powers. We do not wish, however, to lay any stress upon these last observations, some of which we may not have interpreted correctly; but we mention them in order to show that the inequalities that are found to exist between the emergence radiation of various substances promise to be reducible to order as soon as the difficulties of interpretation have been surmounted.

Let us now consider the cathode radiations on the front sides of the plates. Of the cathode particles set free in BC and moving at first in the direction of the  $\gamma$  rays, a certain proportion, say p, is returned by what is beyond. These move towards the face A, and a certain number of them succeed in reaching it and emerging therefrom. In the case of the other plate the proportion returned is p'; the absorption in B'A' is the same as in BA because the weights are the same. Comparing the two plates stratum by stratum, we find that the "incidence" radiation of one plate is to the incidence radiation of the other plate as p to p'. Now p and p' are the well-known constants of the  $\beta$  rays.

When a stream of  $\gamma$  rays is allowed to fall upon a plate, the cathode radiation which issues from the place of incidence must be divisible into two parts. One consists of scattered  $\beta$  particles derived from the stream of such particles which was travelling with the  $\gamma$  rays before incidence, and which was formed during the previous transit of the screens employed—solid, liquid, or gaseous. This part is scattered to an extent which depends on the atomic weight of the plate, according to the usual (McClelland's) law of  $\beta$  particles. The other part is originated in the plate itself in the manner just described, and the amount of it is also regulated according to the  $\beta$ -ray law. When, therefore, observers have measured the secondary radiation due to  $\gamma$  rays, and have found a law corresponding to that for  $\beta$  rays, the reason of the correspondence has been that they really were measuring

the secondary radiation due to  $\beta$  rays. Properly speaking, the secondary radiation produced by  $\gamma$  rays, or rather from  $\gamma$  rays, is proportional to the density of the substance traversed (cf. Wigger's table); and this is only another form of the

law of absorption of y rays.

The relative importance of the two parts of the incidence radiation just mentioned must depend on the circumstances of the experiment\*. The researches of Kleeman (Phil. Mag. Nov. 1907) show very well how the second part, which is influenced by previous screening, modifies the effect of the first part, which is not so influenced, but which follows the law of  $\beta$  rays strictly.

It is easy to show, by comparing corresponding strata at the front and back of one plate, that the incidence radiation should be somewhat less than p times the transmitted radiation,—somewhat less, because the cathode radiation which is turned back is scattered and softened in the process.

To sum up:—

On the ether-pulse theory we ought to find perfect symmetry in the secondary radiations from the two sides of

a plate; but experiment shows nothing of the kind.

On the material, or neutral pair theory, the "incidence" radiations should follow the \(\beta\)-ray law. This is known to be the case. The "emergence" radiations should not follow the  $\beta$ -ray law; and experiment shows that they do not. If the density law held for both  $\beta$  and  $\gamma$  rays, and if the  $\gamma$  rays were homogeneous, the emergence radiations should all be equal. As already explained, experiment shows that the observed inequalities give promise of ready explanation on the ground that no one of these suppositions is quite true.

It is perhaps better not to extend the preliminary account of these experiments by any lengthy discussion of the issues arising from them. Many points that invite consideration have been discussed already in the papers first referred to. Moreover, our own further experiments are incomplete; and their full interpretation is not yet certain. We will therefore confine ourselves to one or two questions which seem to be of special interest.

The X rays resemble the  $\gamma$  rays so closely that it is practically inconceivable that the two radiations should be essentially different. The secondary cathode radiations which are set free when X rays impinge on any material must

<sup>\*</sup> In a recent letter addressed by one of us to 'Nature,' too much stress was laid on the part played by the first part under all circumstances.

therefore have been part of the X-ray stream, and must start their independent existence by moving on in the line of the X-ray motion. Their velocity is much smaller than that of the secondary cathode rays due to  $\gamma$  rays, and they are much more readily scattered. It may still remain an open question whether or no the X-ray stream contains æther pulses. Perhaps their existence must be supposed in order to explain the velocity experiment of Marx, and the diffraction experiment of Haga and Windt. Possibly they are also required in order to explain Barkla's polarization experiments; but we do not think that the experiment described by Barkla in

'Nature' (Oct. 31, 1907) is in any way decisive.

It seems proper to consider a possibility that the negative particle, when it moves on in the original line of motion of the pair from which it came, retains also its original velocity. It is a striking fact that the cathode particle due to the  $\gamma$  rays has the same speed, very nearly, as the  $\beta$  particle issuing from the original radioactive material. And it looks quite unlike a coincidence that similar comparisons can be made in the case of the X rays. The secondary cathode radiations due to these rays have velocities which, at the least, are of the same order as the velocities of the cathode particles in the X-ray bulb. If we examine the table given by Innes (Proc. Roy. Soc. Aug. 2, 1907, p. 461), and if we may be allowed to adopt an interpretation differing somewhat from the author's, but more natural, it seems to us, in view of the conclusions of this paper, we find that the velocities of the electrons emitted by all the metals are practically the same, zinc being an exception because it is unable to break up the hardest rays. We find that the velocities range from about  $6 \times 10^9$  to  $7.5 \times 10^9$  for soft rays, and  $6 \times 10^9$  to  $8 \times 10^9$ for hard rays. Remembering that bundles of X rays are very heterogeneous, the natural conclusion seems to be that the softest rays give the slowest speeds, and that the velocity of the secondary rays increases with the hardness of the X rays from which they are derived. Now the hardness of the rays grows with the speed of the cathode particles in the bulb. Is it then possible that the cathode particle is first set in motion by the electromotive force in the bulb, strikes the anticathode and picks up a positive there, becomes neutral and is now called an X ray, is subsequently stripped of the positive and becomes a secondary cathode particle, the identity of the negative remaining the same throughout and its speed invariable or nearly so? The difficulty comes in when we try to consider the part played by the mass of the positive.

And, again, may not the  $\beta$  and  $\gamma$  forms be interchangeable at times? A  $\gamma$  particle which had been stripped of it

positive and become a secondary cathode or  $\beta$  ray would be lost to measurement as a  $\gamma$  ray; and we should thus have an explanation of how the  $\gamma$  rays are "absorbed," and why the absorption follows an exponential law. And in the same way, if a  $\beta$  particle picked up a positive it would disappear from view as a  $\beta$  particle; it would be "absorbed."

Although we have made a few experiments with magnetic fields, we have not yet come to any conclusion as to whether or no there are  $\gamma$  pairs which have become loosened in the attachment of positive to negative, forming a softer and more ionizing radiation. Their existence might be suspected, since there is an analogous effect in the case of X rays; and probably they would be found more at the back of the penetrated plate than in front of it.

A few further experimental illustrations are shown diagrammatically in figs. 5 and 6 with the explanations

attached.

Fig. 5.—The upper figure shows the general arrangement. The lower figures are diagrammatic, and show the currents for different arrangements of the Pb and Al at the bottom of the chamber, and at the top with the exception of the plate through which the  $\gamma$  rays enter. Inverting the top plates makes little difference when the upper of the two plates at the bottom is Al; but an appreciable difference when it is Pb, because in the latter case a good deal of secondary radiation is thrown up by the Pb, and there is a tertiary from the top plate.

The same, when the conical opening is completely filled

by a Pb stopper:—

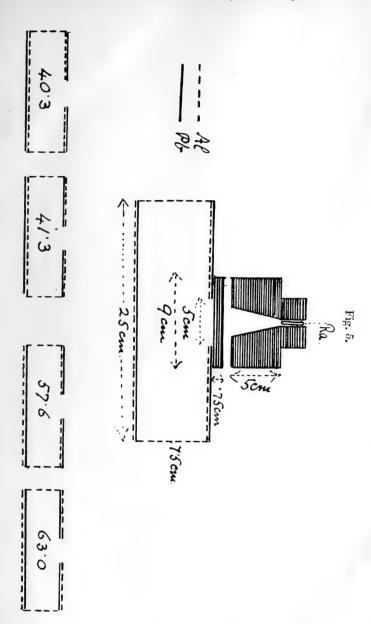
12.6 12.6 17.7 18.3

The differences show the effects of those rays only which are stopped by the Pb stopper:—



These show the effect of inverting that portion only of the top plate where the  $\gamma$  rays enter. Three Pb plates=:55 cm.; Al plate=:16 cm.

The same, with Pb stopper inserted:-



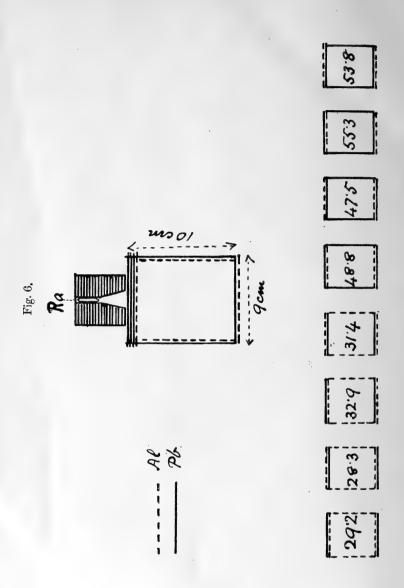


Fig. 6.—The upper figure shows the general arrangement. The wall of the cylindrical vessel was of brass: a Pb or an Al lining could be inserted as shown. The lower figures are diagrammatic, and show the currents for different arrangements of Pb and Al at top, bottom, and sides. Inversion of the plates through which the  $\gamma$  rays pass into the chamber makes little difference; but there is a great change if the material is changed on which the  $\gamma$  rays fall, or the "emergence" radiations from the top plate. The base is of less importance than in fig. 5; but the sides of more importance. This should clearly be so, for geometrical reasons. When the conical opening was filled by a Pb stopper the currents were all reduced considerably, but retained the same proportions pretty nearly.

When a small pencil of  $\beta$  rays was admitted through a hole in the centre of the top plate a change of the material of the bottom became more effective, and of the sides less effective than before; but this difference became smaller when thin Al sheets were so placed as to scatter the  $\beta$  rays

on their entry into the chamber.

In conclusion we should like to add that Wigger was the first, so far as we know, to show clearly that the secondary radiation of Al, on the far side of the plate, was greater than that of Pb. A comparison of the emergence radiations of different metals was made by Dawes (Phys. Rev. xx. p. 182). who showed that they did not follow the law of the incidence The same effect was indicated in the experiments of Eve (Phil. Mag. Dec. 1904). We have little doubt that the interesting experiments of Mackenzie (Phil. Mag. July 1907) are to be explained on the lines indicated in this paper. In fact it is clear that this is the case in a broad sense; but it is difficult to give a complete explanation until the laws are so completely worked out that they can be applied to the interpretation of experiments which are really very complicated, although at first sight they may seem to be simple.

### LXI. Notices respecting New Books.

The Axioms of Projective Geometry and the Axioms of Descriptive Geometry. By A. N. WHITEHEAD, Sc.D., F.R.S. Cambridge University Press, 1907.

THESE tracts, which form Nos. 4 and 5 of the Cambridge Tracts in Mathematics and Mathematical Physics, deal with a branch of mathematics which has lately received much attention from mathematicians, and which, although in its present form of comparatively recent origin, has already attained a high state of development. So important has this subject—the Foundations of Mathematics—become that it is imperative on every mathematician to have some acquaintance with its developments in order to be in sympathy with much of the mathematical work of the present day. Dr. Whitehead's two tracts deal with the geometric side and form an excellent introduction to a detailed study of the whole field. They contain a clear exposition of the foundations of geometry, comprising as much of the theory as is of interest to the general mathematical reader, to whom presumably they are especially intended to appeal. They are, however, equally valuable to the specialist, since they give a fresh and connected view of a subject which is particularly confusing from the variety of ways in which it may be approached.

Theory of Sets of Points. By W. H. Young, M.A., Sc.D., and Grace Chisholm Young, Phil. Doc. (Gott.). Cambridge University Press, 1906.

This is in many respects a unique book. Not only is it the first of its kind which has ever appeared in English, but in no other language apparently has an attempt been made to give a systematic exposition of the subject. The subject itself does not demand on the part of the reader a large stock of mathematical The book may therefore be taken up at almost any point of his mathematical training, probably the sooner the better. After a brief account of rational and irrational numbers and of the manner in which numbers are represented as to order by points on a straight line, the authors enter upon the theory of linear sets and sequences leading up to the conceptions of potency, content, and order. Plane sets are introduced in Chapter VIII.; and in Chapter IX. a succession of theorems deals with the conceptions of region, domain, boundary, and rim, leading up to the definition of a curve. It is here and in the later discussion of plane content and area that the student familiar with the ordinary geometrical assumptions regarding curves and areas will probably for the first time be fully impressed with the value of the theory of sets of points. There can be but one opinion as to the great service rendered by Dr. and Mrs. Young in placing in our hands this systematic treatise on the foundations of mathematics. appendix running to fifteen pages gives the bibliography of the subject.

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#### LONDON, EDINBURGH, AND DUBLIN

## PHILOSOPHICAL MAGAZINE

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## JOURNAL OF SCIENCE.

[SIXTH SERIES.]

JUNE 1908.

LXII. Hamilton's Principle and the Five Aberrations of von Seidel. By Lord RAYLEIGH, O.M., Pres.R.S.\*

L ARGELY owing to the fact that the work of Hamilton, and it may be added of Coddington remainded. in Germany and that of v. Seidel in England, it has scarcely been recognized until recently how easily v. Seidel's general theorems relating to optical systems of revolutions may be deduced from Hamilton's principle. The omission has been supplied in an able discussion by Schwarzschild, who expresses Hamilton's function in terms of the variables employed by Seidel, thus arriving at a form to which he gives the name of Seidel's Eikonal†. It is not probable that Schwarzschild's investigation can be improved upon when the object is to calculate complete formulæ applicable to specified combinations of lenses; but I have thought that it might be worth while to show how the number and nature of the five constants of aberration can be deduced almost instantaneously from Hamilton's principle, at any rate if employed in a somewhat modified form.

When we speak, as I think we may conveniently do, of five constants of aberration, there are two things which we should remember. The first is that the five constants do not stand upon the same level. By this I mean, not merely that some of them are more important in one instrument and some

<sup>\*</sup> Communicated by the Author.

<sup>†</sup> The word Eikonal was introduced by Bruns.

in another, but rather that the nature of the errors is different. In earlier writings the term aberration was, I think, limited to imperfect focusing of rays which, issuing from one point, converge upon another. Three of the five aberrations are of this character; but the remaining two relate, not to imperfections of focusing, but to the position of the focus. It is, in truth, something of an accident that, e. g. in photography, we desire to focus distant objects upon a plane. The second thing to which I wish to refer is that, although Seidel did much, four out of the five aberrations were pretty fully discussed by Airy and Coddington before his time. To these authors is due the rule relating to the curvature of images, generally named after Petzval, so far, at any rate, as it refers to combinations of thin lenses.

Some remarks are appended having reference to systems

of less highly developed symmetry.

According to Hamilton's original definition of the characteristic function V, it represents the time taken by light to pass from an initial point (x', y', z') to a final point (x, y, z), and it may be taken to be  $\int \mu \, ds$ , where  $\mu$  is the refractive index and the integration is along the course of the ray which connects the two points. If the path be varied, the integral is a minimum for the actual ray; and from this it readily follows that

$$l = dV/dx$$
,  $m = dV/dy$ ,  $n = dV/dz$ , (1)

$$-l' = dV/dx', \quad -m' = dV/dy', \quad -n' = dV/dz', \quad (2)$$

where l, m, n, l', m', n' are the direction-cosines of the ray at the end and beginning of its course, the terminal points being situated in a part of the system where the refractive

index is unity.

In his communication to the British Association (B. A. Report, Cambridge 1833, p. 360) Hamilton transforms these equations. As his work is so little known, it may be of interest to quote in full the principal paragraph, with a slight difference of notation:—"When we wish to study the properties of any object-glass, or eye-glass, or other instrument in vacuo, symmetric in all respects, about one axis of revolution, we may take this for the axis of z, and we shall have the equations (1), (2), the characteristic function V being now a function of the five quantities,  $x^2+y^2$ , xx'+yy',  $x'^2+y'^2$ , z, z', involving also, in general, the colour, and having its form determined by the properties of the instrument of revolution. Reciprocally, these properties of the

instrument are included in the form of the characteristic function V, or in the form of this other connected function,

$$T = lx + my + nz - l'x' - m'y' - n'z' - V,$$
 (3)

which may be considered as depending on only three independent variables besides the colour; namely, on the inclinations of the final and initial portions of a luminous path to each other and to the axis of the instrument. Algebraically, T is in general a function of the colour and of the three quantities,  $l^2+m^2$ , ll'+mm',  $l'^2+m'^2$ ; and it may usually (though not in every case) be developed according to ascending powers, positive and integer, of these three latter quantities, which in most applications are small, of the order of the squares of the inclinations. We may therefore in most cases confine ourselves to an approximate expression of the form

$$T = T^{(0)} + T^{(2)} + T^{(4)}, \quad . \quad . \quad . \quad . \quad (4)$$

in which  $T^{(0)}$  is independent of the inclinations;  $T^{(2)}$  is small of the second order, if those inclinations be small, and is of the form

$$T^{(2)} = P(l^2 + m^2) + P_1(ll' + mm') + P'(l'^2 + m'^2); \quad (5)$$

and T<sup>(4)</sup> is small of the fourth order, and is of the form

$$T^{(4)} = Q(l^2 + m^2)^2 + Q_1(l^2 + m^2)(ll' + mm') + Q'(l^2 + m^2)(l'^2 + m'^2) + Q_{11}(ll' + mm')^2 + Q_1'(ll' + mm')(l'^2 + m'^2) + Q''(l'^2 + m'^2)^2; . (6)$$

the nine coefficients,  $PP_1P'QQ_1Q'Q_{11}Q_1'Q''$ , being either constant, or at least only functions of the colour. The optical properties of the instrument, to a great degree of approximation, depend usually on these nine coefficients and on their chromatic variations, because the function T may in most cases be very approximately expressed by them, and because the fundamental equations (1), (2) may rigorously be thus transformed;

$$x - \frac{l}{n}z = \frac{d\mathbf{T}}{dl}, \qquad \iota - \frac{m}{n}z = \frac{d\mathbf{T}}{dm};$$

$$x' - \frac{l'}{n'}z' = -\frac{d\mathbf{T}}{dl'}, \quad y - \frac{m'}{n'}z' = -\frac{d\mathbf{T}}{dm'};$$

$$(7)$$

The first three coefficients, P  $P_1$  P', which enter by (5) into the expression of the term  $T^{(2)}$ , are those on which the focal lengths, the magnifying powers, and the chromatic aberrations depend: the spherical aberrations, whether for

direct or inclined rays, from a near or distant object, at either side of the instrument (but not too far from the axis). depend on the six other coefficients, Q Q<sub>1</sub> Q' Q<sub>11</sub> Q<sub>1</sub>' Q'', in the expression of the term T<sup>(4)</sup>. Here, then, we have already a new and remarkable property of object-glasses, and eye-glasses, and other optical instruments of revolution; namely, that all the circumstances of their spherical aberrations, however varied by distance and inclination, depend (usually) on the values of SIX RADICAL CONSTANTS OF ABER-RATION, and may be deduced from these six numbers by uniform and general processes. And as, by employing general symbols to denote the constant coefficients or elements of an elliptic orbit, it is possible to deduce results extending to all such orbits, which can afterwards be particularized for each; so, by employing general symbols for the six constants of aberration, suggested by the foregoing theory, it is possible to deduce general results respecting the aberrational properties of optical instruments of revolution, and to combine these results afterwards with the peculiarities of each particular instrument by substituting the numerical values of its own particular constants."

Equations (7) are easily deduced. So far as it depends upon the unaccented letters, the total variation of T is

$$d\mathbf{T} = l dx + m dy + n dz + x dl + y dm + z dn$$
$$-\frac{d\mathbf{V}}{dx} dx - \frac{d\mathbf{V}}{dy} dy - \frac{d\mathbf{V}}{dz} dz,$$

or regard being paid to (1),

$$dT = x dl + y dm + z dn,$$

in which

$$l\,dl+m\,dm+n\,dn=0,$$

so that

$$\frac{d\mathbf{T}}{dl} = x - \frac{lz}{n}, \quad \frac{d\mathbf{T}}{dm} = y - \frac{mz}{n};$$

and in like manner by varying the accented letters the second pair of equations (7) follows.

If we agree to neglect the cubes of the inclinations, we may identify n, n' with unity, and (7) becomes

$$\begin{split} x = &(z+2\mathrm{P})l + \mathrm{P}_1 l', & y = &(z+2\mathrm{P})m + \mathrm{P}_1 m', \\ x' = &-\mathrm{P}_1 l + (z'-2\mathrm{P}')l', & y' = &-\mathrm{P}_1 m + (z'-2\mathrm{P}')m', \end{split}$$

determining x, x' in terms of z, z', l, l' supposed known, or conversely l, l' in terms of z, z', x, x' supposed known. The

case of special interest is that in which x, y, z and x', y', z'are conjugate points, i.e. images of one another in the optical system. The ratio x: x' must then be independent of the special values ascribed to l, l'. In order that this may be possible, i. e. in order that z, z' may be conjugate planes, the condition is

$$(z+2P)(z'-2P')+P_1^2=0$$
, . . . (8)

and then

$$\frac{x}{x'} = \frac{y}{y'} = -\frac{z + 2P}{P_1} = \frac{P_1}{z' - 2P'}, \quad . \quad . \quad (9)$$

giving the magnification.

Equations (8), (9) express the theory of a symmetrical instrument to a first approximation. In order to proceed further we should have not only to include the terms in (7) arising from T<sup>(4)</sup>, but also to introduce a closer approximation for n. Thus even though  $T^{(4)}=0$ , we should have additional terms in the expressions for x, x' equal respectively to

$$\frac{1}{2}lz(l^2+m^2)$$
 and  $\frac{1}{2}l'z'(l'^2+m'^2)$ .

If the object is merely to express the aberrations for a single pair of conjugate planes, we may attain it more simply by a modification of Hamilton's process.

Supposing that the conjugate planes are z=0, z'=0, we have V a function of the coordinates of the initial point x', y', and of the final point x, y. And if as before l, m, n', m', n'are the direction-cosines of the terminal portions of the ray, we still have

$$l = dV/dx$$
,  $m = dV/dy$ , . . . (10)

$$l = dV/dx,$$
  $m = dV/dy,$  . . . (10)  
 $l' = -dV/dx',$   $m' = -dV/dy'.$  . . (11)

But now instead of transforming to a function of l, m, l', m', from which x', y', x, y are eliminated, we retain x', y' as independent variables, eliminating only x, y, the coordinates of the final or image point \*. For this purpose we assume

$$U = lx + my - V. \qquad (12)$$

The total variation of U is given by

$$d\mathbf{U} = x dl + l dx + y dm + m dy$$

$$-\frac{d\mathbf{V}}{dx} dx - \frac{d\mathbf{V}}{dy} dy - \frac{d\mathbf{V}}{dx'} dx' - \frac{d\mathbf{V}}{dy'} dy',$$

or with regard to (10), (11)

$$dU = x dl + y dm + l' dx' + m' dy', . . . (13)$$

<sup>\*</sup> Compare Routh's 'Elementary Rigid Dynamics,' § 418.

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from which it appears that U is in reality a function of x', y', l, m. As equivalent to (13), we have

$$x = dU/dl$$
,  $y = dU/dm$ , . . (14)

$$l' = d\mathbf{U}/dx', \qquad m' = d\mathbf{U}/dy'. \qquad . \qquad . \qquad (15)$$

So far U appears as a function of the four variables x', y', l, m; but from its nature, as dependent upon lx + my and V, and from the axial symmetry, it must be in fact a function of the *three* variables

$$x'^2 + y'^2$$
,  $l^2 + m^2$ , and  $lx' + my'$ ,

the latter determining the angle between the directions of x', y' and l, m. When these quantities are small, we may take

 $U = U^{(0)} + U^{(2)} + U^{(4)} + \dots, \qquad (16)$ 

where  $U^{(0)}$  is constant and

$$\mathbf{U}^{(2)} = \frac{1}{2}\mathbf{L}(l^2 + m^2) + \mathbf{M}(x'l + y'm) + \frac{1}{2}\mathbf{N}(x'^2 + y'^2), \quad (17)$$

L, M, N being constants. If we stop at  $U^{(2)}$ , equations (14) give

x = Ll + Mx', y = Lm + My', . . (18)

determining x, y as functions of x', y', l, m. We have next to introduce the supposition that x, y is conjugate to x', y'. Hence L = 0, for to this approximation x, y must be determined by x', y' independently of l, m. Accordingly,

$$x = Mx', \qquad y = My'. \quad . \quad . \quad (19)$$

We are now prepared to proceed to the next approximation. In order to correspond, as far as may be, with the notation of Seidel \* we will write

$$\begin{split} \mathbf{U}^{(4)} &= \frac{1}{4}\mathbf{A}(l^2 + m^2)^2 + \mathbf{B}(l^2 + m^2)(lx' + my') \\ &+ \frac{1}{2}(\mathbf{C} - \mathbf{D})(lx' + my')^2 + \frac{1}{2}\mathbf{D}(l^2 + m^2)(x'^2 + y'^2) \\ &+ \mathbf{E}(lx' + my')(x'^2 + y'^2) + \mathbf{F}(x'^2 + y'^2)^2, \quad . \quad . \quad (20) \end{split}$$

which is the most general admissible function of the

fourth degree.

From (20) we obtain by use of (14) the additional terms in x and y dependent on  $U^{(4)}$ . No generality is lost if at this stage we suppose, for the sake of brevity, y' = 0. Accordingly,

$$x = Al(l^2 + m^2) + Bx'(3l^2 + m^2) + Cx'^2l + Ex'^3$$
, (21)

$$y = Am(l^2 + m^2) + 2Bx'lm + Dx'^2m.$$
 (22)

<sup>\*</sup> Finsterwalder, München. Sitz. Ber. xxvii. p. 408 (1897).

In order to complete the value of x we must add the

expressions in (19) and (21).

Since F disappears from the values of x and y, we see that there are five effective constants of aberration of this order, as specified by Seidel. The evanescence of A is the Eulerian condition for the absence of spherical aberration in the narrower sense, i.e. as affecting the definition of points lying upon the axis (x'=0). If the Eulerian condition be satisfied, B=0 is identical with what Seidel calls the Fraunhofer condition\*. The theoretical investigation of this kind of aberration was one of Seidel's most important contributions to the subject, inasmuch as neither Airy nor Coddington appears to have contemplated it. The conditions A=0, B=0 are those which it is most important to satisfy in the case of the astronomical telescope.

To this order of approximation B=0 is identical with the more general sine condition of Abbe, which prescribes that, in order to the good definition of points just off the axis, a certain relation must be satisfied between the terminal inclinations of the rays forming the image of a point situated on the axis. The connexion follows very simply from the equations already found. By (15), (16), (17), (20), with

m=0,

$$l' = Ml + Bl^3 + \text{terms vanishing with } x', y';$$

so that for the conjugate points situated upon the axis

$$l' = Ml + Bl^3$$
. . . . . (23)

The condition B=0 is thus equivalent to a constant value of the ratio l'/l, that is the ratio of the sines of the terminal inclinations of a ray with the axis. And this is altogether independent of the value of A.

On the supposition that the two first conditions A=0, B=0 are satisfied, we have next to consider the significance

of the terms multiplied by C and D. Since

$$dx/dl = Cx'^2$$
,  $dy/dm = Dx'^2$ ,

we see that C and D represent departures of the primary and secondary foci from the proper plane. In fact if  $1/\rho_1$ ,  $1/\rho_2$ 

\* If A be not equal to zero, it can be shown that the best focussing of points just off the axis requires that

$$Al_0 + Bx' = 0$$

where  $l_0$  is the value of l for the principal ray. For example, if the optical system reduces to a combination of thin lenses close together,  $l_0 = x/f$ , where f is the distance of the lenses from the image plane. Since by (19), x = Mx', the condition may be written

$$AM + Bf = 0$$
.

be the curvatures of the images, as formed by rays in the two planes,

$$1/\rho_1 = 2C$$
,  $1/\rho_2 = 2D$ . . . (24)

The condition of astigmatism is then

$$C = D$$
; . . . . . (25)

but unless both constants vanish the image is curved.

Finally the term containing E represents distortion.

If we impose no restriction upon the values of the constants of aberration, we have in general from (21), (22)

$$dx/dl = A(3l^2 + m^2) + 6Bx'l + Cx'^2,$$
  
 $dy/dm = A(l^2 + 3m^2) + 2Bx'l + Dx'^2.$ 

These equations may be applied to find the curvatures of the image as formed by rays infinitely close to given rays, as for example when the aperture is limited by a narrow stop placed centrally on the axis, but otherwise arbitrarily. The principal ray is then characterized by the condition m=0, and we have

$$dx/dl = 3Al^2 + 6Bx'l + Cx'^2 = 3H + K$$
, . . (26)

$$dy/dm = Al^2 + 2Bx'l + Dx'^2 = H + K$$
, . . . (27)

equations which determine the curvatures of the images as formed by rays in the neighbourhood of the given one, and deviating from it in the primary and secondary planes respectively.

According to (26), (27),

$$2H = 2Al^2 + 4Bx'l + (C-D)x'^2$$
, . . . (28)

$$2K = (3D - C)x^{2}$$
. . . . . (29)

The requirement of flatness in both images is thus satisfied if H=0, K=0. The former is the condition of astigmatism, and it involves the ratio of x':l, which is dependent upon the position of the stop; but the latter does not depend on this ratio. It corresponds to the condition formulated by Coddington and later by Petzval. From (28), (29) we may of course fall back upon the conditions already laid down for the case where A=0, B=0.

The further pursuit of this subject requires a more particular examination of what occurs when light is refracted at spherical surfaces. Reference may be made to Schwarzschild\*, who uses Hamilton's methods as applied to a special form of the characteristic function designated as Seidel's Eikonal. A concise derivation of the Coddington-Petzval

<sup>\*</sup> Göttingen Abh. iv. 1905.

condition by elementary methods will be found in Whittaker's tract  $^*$ .

Before leaving systems symmetrical about an axis to which all the rays are inclined at small angles, we may remark that, as  $\dot{U}^{(4)}$  contains 6 constants, in like manner  $\dot{U}^{(6)}$  contains 10 constants † and  $\dot{U}^{(8)}$  15 constants, of which in each case one is ineffective.

The angle embraced by some modern photographic lenses is so extensive that a theory which treats the inclinations as small can be but a rough guide. It remains true, of course, that an absolutely flat field requires the fulfilment of the Coddington-Petzval condition; but in practice some compromise has to be allowed, and this involves a sacrifice of complete flatness at the centre of the image. It will be best to fulfil the conditions dx/dl = 0, dy/dm = 0, or, what are equivalent,

$$d^2 U/dl^2 = 0$$
,  $d^2 U/dm^2 = 0$ ,

not when l is very small but when it attains some finite specified value. If we suppose y'=0, U is a function of  $x'^2$ ,  $l^2+m^2$ , and lx', or say of u, v, w. Hence

$$\begin{split} \frac{d^2 \mathbf{U}}{dl^2} &= 4 l^2 \frac{d^2 \mathbf{U}}{dv^2} + 2 \frac{d \mathbf{U}}{dv} + x'^2 \frac{d^2 \mathbf{U}}{dw^2} + 4 x' l \frac{d^2 \mathbf{U}}{dw \ dv}, \\ \frac{d^2 \mathbf{U}}{dm^2} &= 4 m^2 \frac{d^2 \mathbf{U}}{dv^2} + 2 \frac{d \mathbf{U}}{dv}. \end{split}$$

After the differentiations are performed, we are to make m=0; so that the two conditions of astigmatism and focus upon the plane, analogous to (28), (29), are

$$\frac{d\mathbf{U}}{dv} = 0$$
,  $4l^2 \frac{d^2\mathbf{U}}{dv^2} + x'^2 \frac{d^2\mathbf{U}}{dw^2} + 4x'l \frac{d^2\mathbf{U}}{dv dw} = 0$ ,

in which v is to be made equal to  $l^2$ . But it is doubtful whether such equations could be of service.

Let us now suppose that the system is indeed symmetrical with respect to the two perpendicular planes of x and y, but not necessarily so round the axis of z. In the expression for U no terms can occur which would be altered by a simultaneous reversal of x' and l, or of y' and m. For  $U^{(2)}$  we have

$$U^{(2)} = \alpha l^2 + \beta m^2 + \gamma x' l + \delta y' m$$
+ terms independent of  $l$  and  $m$ .

<sup>\* &#</sup>x27;Theory of Optical Instruments,' Cambridge, 1907. The optical invariants, introduced by Abbe, are there employed.

† Schwarzschild, loc. cit.

686 Hamilton's Principle and the Five Aberrations of v. Seidel. Hence, by (14),

$$x = 2\alpha l + \gamma x', \quad y = 2\beta m + \delta y'.$$

If x, y is conjugate to x', y', we must have

$$\alpha = 0, \quad \beta = 0;$$

so that

$$x = \gamma x', \quad y = \delta y'. \quad . \quad - \quad . \quad (30)$$

These are the equations of the first approximation, and they indicate that the magnification need not be the same in the two directions.

There are no terms in  $U^{(3)}$ . As regards  $U^{(4)}$ , we have

In (31) there are 16 effective constants as compared with 5 in the case where the symmetry round the axis is complete; so that such symmetry implies 11 relations among the constants of (31). For example, in the terms of the first line representing Eulerian aberration, axial symmetry requires that

$$C = \frac{1}{2}B = A$$
. . . . . (32)

We will next suppose that the only symmetry to be imposed is that with respect to the primary plane y=0; so that U is unchanged if the signs of y' and m are both reversed.  $U^{(2)}$  is of the same form as in the case of double symmetry, and

$$x = 2\alpha l + \gamma x', \quad y = 2\beta m + \delta y'.$$

If x, y is the image of x', y', formed by rays in both planes,  $\alpha = 0$ ,  $\beta = 0$ , as before. But it may happen, e. g. in the spectroscope, that there is astigmatism even in the first approximation. If the points are images of one another as constituted by rays in the *primary* plane,  $\alpha = 0$ , but  $\beta$  is left arbitrary.

The next term in U may be denoted by  $U^{(3)}$ . If no conditions of symmetry were imposed,  $U^{(3)}$  would include 16 effective terms, *i. e.* terms contributing to x, y; but the

symmetry with respect to y=0 excludes 8 of these. We may write

$$U^{(3)} = al^{3} + blm^{2} + cx'l^{2} + dx'm^{2} + ey'lm + fx'^{2}l + gx'y'm + hy'^{2}l, \qquad (33)$$

and, by (14),

$$x = 3al^{2} + bm^{2} + 2cx'l + ey'm + fx'^{2} + hy'^{2}.$$
 (34)

If the rays all proceed from the point x'=0, y'=0, the conditions for a well-formed primary focal line are

$$a = 0, \quad b = 0, \quad \dots \quad (35)$$

of which the first expresses that there is no aberration of this order for rays in the primary plane, *i. e.*, that the focal line is *thin*, while the second is the condition that the focal line is *straight* \*.

But if, while x'=0, y' be left arbitrary, so that the source of light is linear, the evanescence of (34) requires, in addition

to (35), that

$$e = 0, \quad h = 0.$$
 . . . (36)

Terling Place, Witham, April 20, 1908.

# LXIII. The Problem of a Spherical Gaseous Nebula. By the late Lord Kelvin†.

This paper was begun about the close of 1906, in order to fulfil a promise given at the end of the paper "On the Convective Equilibrium of a Gas under its own Gravitation only," published in the Philosophical Magazine, 1887; and part of it was communicated by Lord Kelvin to the Royal Society of Edinburgh at its meeting on the 21st January 1907. Since then, however, important additions have been made to it, and the subject has been dealt with more fully than was originally intended. Unfortunately the manuscript was left incomplete at Lord Kelvin's death. It ended with § 35.

However, from information which I received from Lord Kelvin while carrying out the earlier work connected with the paper, I have been able to write the sections from § 36 to the end. These complete all that Lord Kelvin desired to include in this communication;

<sup>\*</sup> Compare Phil. Mag. vol. viii. p. 481, 1879; Scientific Papers, i. p. 440.

+ Communicated by Dr. J. T. Bottomley, F.R.S.

and they express, I believe, the views he held while writing the earlier sections.

The statement of mathematical solutions and numerical results separately, as an Appendix to the paper, under my own name, is in accordance with Lord Kelvin's wishes.

George Green, Secretary.

§ 1.\* IF a fluid globe were given with any arbitrary distribution of temperature, subject only to the condition that it is uniform throughout every spherical surface concentric with the boundary, the cooling, by radiation into space, and consequent augmentation of density of the fluid at its boundary, would immediately give rise to an instability according to which some parts of the outermost portions of the globe would sink, and upward currents would consequently be developed in other portions. In any real fluid, whether gaseous or liquid, this kind of automatic stirring would tend to go on until a condition of approximate equilibrium is reached, in which any portion of the fluid descending or ascending would, by the thermodynamic action involved in change of pressure, always take the temperature corresponding to its level, that is to say, its distance from the centre of the globe. The condition thus reached, when heat is continually being radiated away from the spherical boundary, is not perfect equilibrium. It is only an approximation to equilibrium, in which the temperature and density are each approximately uniform at any one distance from the centre, and vary slowly with time, the variable irregular convective currents being insufficient to cause any considerable deviation of the surfaces of equal density and temperature from sphericity.

§ 2. The problem of the convective equilibrium of temperature, pressure, and density, in a wholly gaseous, spherical fluid mass, kept together by mutual gravitation of its parts, was first dealt with by the late Mr. Homer Lane, who, as we are told by Mr. T. J. J. See, was for many years connected with the U.S. Coast and Geodetic Survey at Washington. His work was published in the American Journal of Science, July 1870, under the title "On the Theoretical Temperature"

of the Sun" †.

\* § 1 is extracted from "On Homer Lane's Problem of a Spherical

Gaseous Nebula," Nature, Feb. 14, 1907.

† The real subject of this paper is that stated in the text above. The application of the theory of gaseous convective equilibrium to sun heat and light is very largely vitiated by the greatness of the sun's mean density (1.4 times the standard density of water). Common air, oxygen, and carbonic acid gas show resistance to compression considerably in

In a letter to Joule, which was read before the Literary and Philosophical Society of Manchester, January 21, 1862, and published in the Memoirs of the Society under the title, "On the Convective Equilibrium of Temperature in the Atmosphere" \*, it was shown that natural up and down stirring of the earth's atmosphere, due to upward currents of somewhat warmer air, and return downward flow of somewhat cooler air, in different localities, causes the average temperature of the air to diminish from the earth's surface upwards to a definite limiting height, beyond which there is no air. It was also shown that, were it not for radiation of heat across the air, outwards from the earth's surface. and inwards from the sun, the temperature of the highly rarefied air close to the bounding surface would be just over absolute zero; that is to say, temperature and density would come to zero at the same height as we ideally rise through the air to the boundary of the atmosphere. Homer Lane's problem gives us a corresponding law of zero density and zero temperature, at an absolutely defined spherical bounding surface (see § 27 below). In fact it is clear that if in Lane's problem we first deal only with a region adjoining the spherical boundary, and having all its dimensions very small in comparison with the radius, we have the same problem of convective equilibrium as that which was dealt with in my letter to Joule.

§ 3. According to the definition of "convective equilibrium" given in that letter, any fluid under the influence of gravity is said to be in convective equilibrium if density and temperature are so distributed throughout the whole fluid mass that the surfaces of equal temperature, and of

\* Republished in Sir William Thomson's Math. and Phys. Papers,

vol. iii. p. 255.

excess of the amount calculated according to Boyle's Law, when compressed to densities exceeding four, or five, or six, tenths of the standard density of water. There seems strong reason to believe that every fluid whose density exceeds a quarter of the standard density of water resists compression much more than according to Boyle's Law, whatever be the temperature of the fluid, however high, or however low. We may consider it indeed as quite certain that a large proportion of the sun's interior, if not indeed the whole of the sun's mass within the visible boundary, resists compression much more than according to Boyle's Law. It seems indeed most probable that the boundary, which we see when looking at the sun through an ordinary telescope, is in reality a surface of separation between a liquid and its vapour; and that all the fluid within this boundary resists compression so much more than according to Boyle's Law that it does not even approximately satisfy the conditions of Homer Lane's problem; and that in reality its density increases inwards to the centre vastly less than according to Homer Lane's solution (see § 56 below).

equal pressure, remain unchanged when currents are produced in it by any disturbing influence so gentle that changes of pressure due to inertia of the motions are negligible. The essence of convective equilibrium is that if a small spherical or cubic portion of the fluid in any position P is ideally enclosed in a sheath impermeable to heat, and expanded or contracted to the density of the fluid at any other place P', its temperature will be altered, by the expansion or contraction, from the temperature which it had at P, to the actual temperature of the fluid at P'. The formulas to express this condition were first given by Poisson. They are now generally known as the equations of adiabatic expansion or contraction, so named by Rankine. They may be written as follows, for the ideal case of a perfect gas:—

$$\frac{p}{p'} = \left(\frac{\rho}{\rho'}\right)^k \qquad . \qquad . \qquad . \qquad . \qquad (1);$$

$$\frac{\rho}{\rho'} = \left(\frac{t}{t'}\right)^{\frac{1}{k-1}} \dots \dots \dots (2);$$

where  $(t, \rho, p)$ ,  $(t', \rho', p')$  denote the temperatures, densities, and pressures, at any two places in the fluid (temperatures being reckoned from absolute zero); and k denotes the ratio of the thermal capacity of the gas when kept at constant pressure to its thermal capacity at constant volume, which, according to a common usage, is for brevity called "the ratio of specific heats." For dry air, at any temperature, and at any density within the range of its approximate fulfilment of the gaseous laws, we have

$$k=1.41$$
;  $\frac{k-1}{k}=.291$ ;  $\frac{k}{k-1}=3.44$  . . (4).

For monatomic gases we have

$$k = \frac{5}{3}; \quad \frac{k-1}{k} = \frac{2}{5}; \quad \frac{k}{k-1} = \frac{5}{2} \quad . \quad . \quad (5).$$

For real gases, we learn from the Kinetic Theory of Gases, and by observation, that k may have any value between 1 and  $1\frac{2}{3}$ , but that it cannot have any value greater than  $1\frac{2}{3}$ , or less than 1.

§ 4. To specify fully the quality of any gas, so far as concerns our present purpose, we need, besides k, the ratio of its specific heats, just one other numerical datum, the volume of a unit mass of it at unit temperature and unit

pressure. This, which we shall denote by S, is commonly called the specific volume; and its reciprocal, 1/S, we shall call the specific density (D) of the gas. In terms of this notation, the Boyle and Charles gaseous laws are expressed by either of the equations

$$pv = St$$
 ... (6), or  $p = \rho St$  ... (6');

where  $p, v, \rho$ , denote respectively the pressure, the volume of unit mass, and the density of the gas at temperature t, reckoned from absolute zero. Our unit of temperature throughout the present paper will be  $273^{\circ}$  C. Thus the Centigrade temperature corresponding to t in our notation is 273(t-1).

§ 5. In virtue of § 4, what is expressed by (1), (2), (3), equivalent as they are to two equations, may now, for working purposes, be expressed much more conveniently by the single formula (6), together with the following equation—

$$p = A \rho^k \qquad . \qquad . \qquad . \qquad . \qquad (7)$$

where A denotes what we may call the Adiabatic Constant, which is what the pressure would be, in adiabatic convective equilibrium, at unit density, if the fluid could be gaseous at

so great a density as that.

§ 6. Looking to (6), remark that p being pressure per unit of area, the dimensions of pv are  $L^{-2} \times L^3$  or L, if we express force in terms of an arbitrary unit, as in § 10 below; therefore S, though we call it specific volume, is a length. It is in fact, as we see by (9) below, equal to the height of the homogeneous atmosphere at unit temperature, in a place for which the heaviness of a unit mass is the force which we call unity in the reckoning of p.

§ 7. In the definition of what is commonly called the "height of the homogeneous atmosphere," and denoted by H, an idea very convenient for our present purpose is introduced. Let p be the pressure and  $\rho$  the density, at any point P within a fluid, liquid or gaseous, homogeneous or heterogeneous, in equilibrium under the influence of mutual gravitation between its parts; and let g be the gravitational attraction on a unit of mass at the position P. Let

$$g\rho H = p$$
 . . . . . (8)

This means that H is the height to which homogeneous liquid, of uniform density  $\rho$ , ideally under the influence of uniform gravity equal to g, must stand in a vertical tube to give pressure at its foot equal to p.

§ 8. The idea expressed by (8) is useful in connection with

questions connected with internal pressure throughout a spherical liquid mass, such as the sun. It is also useful when we are considering pressure and temperature in gaseous fluids, such as our terrestrial atmosphere, or the outermost parts of the sun; which may be regarded as practically gaseous where the density is anything less than 1. § 9. For a perfect gas, (8) divided by  $\rho$ , becomes

gH = St . . . . . (9).

By this we see, what is interesting to remark, that for the same temperature and same gaseous material, the "height of the homogeneous atmosphere" is the same for the air at the earth's surface and for the air at any height above the surface; and is the same for different barometric pressures. For different temperatures, it varies as the absolute temperature. For different gases at the same temperature, it is proportional to their specific volumes. For different forces

of gravity, it is inversely proportional to them.

§ 10. Even for cosmical reckonings in respect to our present subject, and in many and varied terrestrial reckonings, it is convenient to take as unit of force the heaviness in mid-latitudes of the unit of mass. The unit of mass, for all nations and peoples of the earth, must for general convenience be founded on the existing French Metrical System. The unit may, according to the particular magnitude or character of substance of which the mass or quantity is to be specified, be conveniently taken as a milligram, or a gram, or a kilogram, or a metric ton (one thousand kilograms), or 10<sup>9</sup> tons.

§ 11. The choice of unit force as mean terrestrial heaviness of unit mass is very convenient for ordinary earthly purposes, but language in which it is adopted is, unless properly guarded and tacitly understood, always liable to ambiguity as to whether force or quantity of matter is meant. if (using for a moment the moribund British Engineering reckonings in pounds, inches, etc.) we speak of 73 pounds of lead, there is no doubt that we mean quantity of a particular kind of matter; but if we speak of 73 pounds per square inch (which might be 73 pounds of lead, or of iron, or of stone) we mean a force. If we call the pressure on the boiler of a ship 73 pounds per square inch, we mean a somewhat greater pressure when the ship is in middle or northern latitudes than when she is on the equator; though the difference is, for pressures on safety-valves, practically negligible, being for example three-tenths per cent. between the equator and the latitude of Glasgow or Edinburgh.

§ 12. In the present paper we shall take as unit of mass the mass of a cubic kilometre of water at standard density (which is 109 metric tons); and we shall take its heaviness in mid-latitudes as unit of force. This means taking for g in (8) and (9), and in all future formulas, the ratio of gravity at the place under consideration to terrestrial gravity in mid-latitudes. Hence (remembering that in § 4 we have chosen for our unit temperature reckoned from absolute zero the temperature of melting ice, being equal to 273° Centigrade above absolute zero) we see by (8) that S is simply the height in kilometres of the Homogeneous Atmosphere in mid-latitudes, at the freezing temperature. Thus, from known measurements of densities, we have the following table \* of values of S for several different gases :-

Gas.			S.
Air			7.988 kilometres.
Ammonia			13.414
Argon			5.767 ,,
Carbon dioxide			5.232
Carbon monoxide			8.370 ,,
			3.297 ,,
Helium			
Hydrogen			114.76 ,,
Nitrogen			
Oxygen		٠	7.233 ,,
Sulphur dioxide	•	•	3.709 ,,

§ 13. Consider now convective equilibrium in any part of a wholly gaseous globe, or in any part of a fluid globe so near the boundary as to have density small enough to let it fulfil the gaseous laws. Let z be depth measured inwards from any convenient point of reference. The differential equation of fluid equilibrium is

$$dp = g\rho dz$$
 . . . . (10).

Now, if the equilibrium is convective, we have by (3)

$$dp = \frac{k}{k-1} \frac{p'}{t'} \left(\frac{t}{t'}\right)^{\frac{1}{k-1}} dt$$
 . . . (11).

Using this, and (2), in (10), and dividing both members by  $\left(\frac{t}{t'}\right)^{\frac{1}{k-1}}$ , we find  $\frac{dt}{dz} = \frac{k-1}{k} \frac{g\rho't'}{p'} \qquad (12).$ 

<sup>\*</sup> If instead of taking 10° tons as our unit of mass we take a gram, the numbers in this table must each be multiplied by 10°, and they will then be the values of S in centimetres instead of in kilometres.

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Whence, by (6), we find

$$\frac{dt}{dz} = \frac{k-1}{k} \frac{g}{8} \qquad (13);$$

and, (2) repeated

$$\frac{\rho}{\rho'} = \left(\frac{t}{t'}\right)^{\frac{1}{k-1}} \quad . \quad . \quad . \quad . \quad . \quad (14).$$

§ 14r These are exceedingly important and interesting results. By (13) we see that in any part of a wholly gaseous spherical nebula, or in a gaseous atmosphere around a solid or liquid nucleus, in convective equilibrium, sufficiently stirred to have the same chemical constitution throughout, the temperature-gradient of increase inwards is in simple proportion to the force of gravity at different distances from the centre. We also see that in gaseous spherical nebulas of different chemical constitutions, or in gaseous atmospheres of different chemical constitutions, around solid or liquid nucleuses, the temperature-gradients at places of the same gravity are simply proportional to the values of (k-1)/(kS) for the different gases or gaseous mixtures.

§ 15. For the terrestrial atmosphere we have by (4)  $\frac{k}{k-1} = 3.44$ , and by the table in § 12, S=7.988 kilometres.

The temperature-gradient according to (13) is therefore, at the rate of our unit of temperature, or 273 degrees Centigrade, per 27.5 kilometres; or 1° C. in 100.6 metres. This is much greater than the temperature-gradient found by Welsh, in balloon ascents of about fifty years ago, which was only 1° C. in 161 metres \*. Joule, with whom I had been in discussion on the subject in 1862, suggested to me that the discrepance might be accounted for by the condensation of vapour in upward currents of air. In endeavouring to test this suggestion, I made some calculations of which results are shown in the following table, extracted from a table given in my paper of 1862, referred to in § 2 above.

<sup>\*</sup> Mr. Shaw informs me that much investigation in later times gives a general average mean gradient of  $1^{\circ}$  C. per 164 metres. This is very nearly the same as it would be with no disturbance from radiation in air saturated with moisture, at  $4^{\circ}$  C.

Temperature centigrade or $t-273.7$ .	Elevation from Earth's surface required to cool moist air by 1° C.
	$\frac{dx}{-dt}$
0	Metres 152
5	168
10	186
15	207
20	229
25	252
30	274
35	284

§ 16. From this we see that an ascending current of moist air at 3° C. would sink in temperature at about the rate of 1° C. in 161 metres of ascent. This is exactly Welsh's gradient; "and we may conclude that at the times and places of his observations the lowering of temperature upwards was nearly the same as that which air saturated with moisture [at 3° C.] would experience in ascending "\*. But it is not to be supposed, indeed it cannot have been the case, that his observations were made in a single ascent through cloud. "It is to be remarked that except when the air is saturated, and when, therefore, an ascending current will always keep forming cloud, the effect of vapour of water, however near saturation, will be scarcely sensible on the cooling effect of expansion".

§ 17. But, considering our terrestrial atmosphere as a whole, and the complicated circumstances of winds, and rain, and snow, and its heatings by radiations from the sun, and its coolings by radiation into starlit space, and its heatings and coolings by radiations to land and sea in different latitudes, we may feel sure that Joule's suggestion shows a cause contributing importantly to the general average temperature-gradient being less than it would be in dry air in

convective equilibrium.

§ 18. For the solar atmosphere, we have approximately, q=28 (28 times middle latitude gravity at the earth's surface).

<sup>\*</sup> Quoted from the Manchester paper above referred to, Math. and Phys. Papers, vol. iii. p. 260.
† Ibid.

By way of example, we may take S and k the same as for the terrestrial atmosphere, as we have not sufficient knowledge from spectrum analysis to allow us to guess other probable values of S and k for the mixture of gases constituting the upper parts of the sun's atmosphere, than those we know for the mixture of Oxygen, Nitrogen, Argon, and Carbonic Acid, which in the main constitutes our terrestrial atmosphere. Thus in the upper atmosphere of the sun, if in purely convective equilibrium, and undisturbed by radiations and other complications, the temperature would increase at the rate of 280 degrees Centigrade per kilometre downwards, and, looking forward to § 27 below, we see that the increase of temperature would start from absolute zero at the boundary, where density, pressure, and temperature, are all zero. It would require very robust faith in the suggestion of convective equilibrium for the gaseous atmosphere of the sun to believe in +7° C. being the actual temperature of the sun's atmosphere at one kilometre below the boundary. I am afraid I cannot quite profess that faith. It seems to me that the enormous radiation from below would, if the upward and downward currents were moderately tranquil, overheat the air in the uppermost kilometre of the sun's atmosphere to far above the temperatures ranging from -273° Centigrade to +7° Centigrade, calculated as above from the adiabatic convective theory.

§ 19. Keeping, however, for the present by way of example, to the calculated results of this theory, with the data for S and k chosen in § 15, we find at ten and at fifty kilometres below the boundary, the temperatures, reckoned in Centigrade degrees above absolute zero, would be respectively 2800 and 14000. Calling these temperatures t' and t, and the densities at the same places  $\rho'$  and  $\rho$ , we find by (14)

$$\frac{\rho}{\rho'} = \left(\frac{14,000}{2800}\right)^{\frac{5}{2}} = 55.9$$
 . (15).

Suppose for example  $\rho'$  to be '001 (1/1000 of the density of water), we shall have  $\rho = 056$ . This last is nearly but not quite too great a density for approximate fulfilment of the gaseous laws for the same gaseous mixture as our air. Thus, if not too much disturbed by radiation of heat from below, the uppermost fifty kilometres of the sun's atmosphere might be quite approximately in gaseous convective equilibrium; with density and temperature augmenting from zero at the boundary, to density '056, and temperature 14000 Centigrade degrees above absolute zero, at the fifty kilometres

depth. But, going down fifty kilometres deeper, we find that the temperature at one hundred kilometres depth would be 28000°, and the density would be 316. This density is much too great to allow even an approximate fulfilment of the gaseous laws, by any substance known to us, even if its temperature were as high as 28000°. This single example is almost enough to demonstrate that the approximately gaseous outer shell of the sun cannot be as much as 100 kilometres thick—a conclusion which may possibly be tested, demonstrated, or contradicted, by sufficiently searching spectroscopic analysis. The character of the test would be to find the thickness of the outermost layer from which the bright spectrum lines proceed. If it were '1" as seen from the earth, it would be 73 kilometres thick.

§ 20. Considering the great force of gravity at the sun's surface (about 28 times terrestrial gravity), it is scarcely possible to conceive that any fluid, composed of the chemical elements known to us, could be gaseous in the sun's atmosphere at depths exceeding one hundred kilometres. I am forced to conclude that the uppermost luminous bright-line-emitting layer of our own sun's atmosphere, and of the atmosphere of any other sun of equal mass, and of not greater radius, cannot probably be as much as one hundred kilometres thick.

§ 21. There must have been a time, now very old, in the history of the sun when the gravity at his boundary was much less than 28, and the thickness of his bright-lineemitting outermost layer very much greater than one hundred kilometres. Going far enough back through a sufficient number of million years, in all probability we find a time when the sun was wholly a gaseous spherical nebula from boundary to centre, and a splendid realization of Homer Lane's problem. The mathematical solution of Homer Lane's problem will, for a spherical gaseous nebula of given mass, tell exactly what, under the condition of convective equilibrium, the density and temperature were at any point within the whole gaseous mass, when the central density was of any stated amount less than '1; on the assumption that we know the specific volume (S) and the ratio of specific heats (k) for the actual mixture of gases constituting the nebula. It will also allow us to find, at the particular time when any stated quantity of heat has been radiated from the gaseous nebula into space, exactly what its radius was, what its central temperature and density were, and what were the temperature and density at any distance from the centre. Thus, on the assumption of S and k known, we have a complete history

of the sun (or any other spherical star) for all the time before

the central density had come to be as large as 1.

§ 22. To pass from the case of convective equilibrium in a gaseous atmosphere so thin that the force of gravity is practically constant throughout its thickness, to the problem of convective equilibrium through any depth, considerable in comparison with the radius, or through the whole depth down to the centre, provided the fluid is gaseous so far, we have only to use (13) and (14), with the proper value of g, varying according to distance from the centre. Remembering that we are taking g in terms of terrestrial gravity, and that the mean density of the earth is 5·6, in terms of the standard density of water, which we are taking as our unit density, we have the following expression for g, in any spherical mass, m, having throughout equal densities,  $\rho$ , at equal distances, r, from the centre:—

$$g = \frac{m/r^2}{E/e^2} = \frac{3}{5 \cdot 6.e} \frac{\int_0^r dr \, r^2 \rho}{r^2} \quad . \quad . \quad . \quad (16),$$

where E denotes the earth's mass, and e the earth's radius. This expression we find by taking g as the force of gravity due to matter within the sphere of radius r, according to Newton's gravitational theorem, which tells us that a spherical shell of matter having equal density throughout each concentric spherical surface exerts no attraction on a point within it. Using this in (13) of § 13, with dz = -dr; multiplying both members by  $r^2$ , and introducing m to denote the mass of matter within the spherical surface of radius r, we find

$$-r^2 \frac{dt}{dr} = \frac{3}{5 \cdot 6.e} \frac{k-1}{kS} \int_0^r dr \, r^2 \rho = \frac{3}{5 \cdot 6.e} \frac{k-1}{kS} \frac{m}{4\pi} \quad . \quad (17).$$

Differentiating (17) with reference to r, we find

$$-\frac{d}{dr}\left[r^2\frac{dt}{dr}\right] = \frac{3}{5\cdot 6.e}\frac{k-1}{kS}r^2\rho \quad . \quad . \quad (18)$$

§ 23. By (6), and (7), of §§ 4, 5, we find

$$\rho = \left(\frac{\mathrm{S}t}{\mathrm{A}}\right)^{\kappa} \quad . \quad . \quad . \quad . \quad (19),$$

where

$$\kappa = \frac{1}{k-1} \quad . \quad . \quad . \quad . \quad (20).$$

Eliminating  $\rho$  from (18) by (19), we find

$$-\frac{d}{dr}\left[r^2\frac{dt}{dr}\right] = \frac{r^2t^{\kappa}}{\sigma^2} \quad . \quad . \quad . \quad (21),$$

where

$$\sigma^2 = \frac{5 \cdot 6 \cdot e(\kappa + 1) A^{\kappa}}{3S^{\kappa - 1}} \qquad . \qquad . \qquad (22).$$

§ 24. By putting

$$r = \frac{\sigma}{x} \quad . \quad . \quad . \quad . \quad . \quad . \quad (23),$$

we reduce (21) to the very simple form,

$$\frac{d^2t}{dx^2} = -\frac{t^{\kappa}}{x^4} \quad . \quad . \quad . \quad (24);$$

the equation of the first and third members of (17), modified by (20) and (23), gives

$$\frac{m}{E} = \frac{(\kappa + 1)S\sigma}{e^2} \frac{dt}{dx} \quad . \quad (25)$$

§ 25. Let  $t = \Re(x)$  be any particular solution of this equation; we find as a general solution, with one disposable constant C,

 $t = C_{\mathfrak{F}}[xC^{-\frac{1}{2}(\kappa-1)}] \dots (26),$ 

which we may immediately verify by substitution in (24). Here  $\mathfrak{F}(x)$  may denote a solution for a gaseous atmosphere around a solid or liquid nucleus, or it may be the solution for a wholly gaseous globe, in which case  $\mathfrak{F}(x)$  will be finite, and  $\mathfrak{F}'(x)$  will be zero, when  $x=\infty$ . Each solution  $\mathfrak{F}(x)$  must belong to one or other of two classes:—

Class A: that in which the density increases continuously from the spherical boundary to a finite maximum at the centre. In this class we have  $d\rho/dr=0$  (dt/dr=0), when r=0; or, which amounts to the same,  $d\rho/dx=0$  (dt/dx=0),

when  $x = \infty$ .

Class B: that in which, in progress from the boundary inwards, we come to a place at which the density begins to diminish, or is infinite; or that in which the density increases

continuously to an infinite value at the centre.

With units chosen to make  $\mathfrak{F}(\infty)=1$ , we shall denote the function  $\mathfrak{F}$  of class A by  $\Theta_{\kappa}$ , and call it Homer Lane's Function; because he first used it, and expressed in terms of it all the features of a wholly gaseous spherical nebula in convective equilibrium, and calculated it for the cases,  $\kappa=1.5$  and  $\kappa=2.5$  ( $k=1\frac{2}{3}$  and k=1.4). He did not give tables of

numbers, but he represented his solutions by curves \*. He did give some of his numbers for three points of each curve, and Mr. Green, by very different methods of calculation, has found numbers for the case  $\kappa = 2.5$ , agreeing with them to within  $\frac{1}{10}$ th per cent.

§ 26. By improvements which Mr. Green has made on previous methods of calculation of Homer Lane's Function, and which he describes in an Appendix to the present paper, he has calculated values of the function  $\Theta_{\kappa}(x)$ , and of its differential coefficient  $\Theta'_{\kappa}(x)$ , which are shown in five tables corresponding to the following five values of  $\kappa$ , 1.5, 2.5, 3, 4,  $\infty$ . For the four finite values of  $\kappa$  the practical range of each table is from x=q to  $x=\infty$ , q denoting the value of x which makes t=0.

§ 27. There is such a value of x which is real in every case in which  $\kappa$  is positive and less than 5. This we see exemplified in the four diminishing values of q found by Mr. Green (2737, 1867, 1450, 0667) † for the four finite values of  $\kappa$ , 1.5, 2.5, 3, 4, and in the zero value of q for  $\kappa = 5$ , the case described in § 29 below. In this case equation (24) has a solution in finite terms, which gives  $t = \sqrt{3} \cdot x$  for infinitely small values of x, and therefore makes q = 0 for x = 0.

§ 28. Two interesting cases,  $\kappa = 1$  and  $\kappa = 5$ , for each of which the differential equation (24) is soluble in finite terms, have been noticed, the former by Ritter ‡, the latter by Schuster §. Ritter's case yields in reality Laplace's celebrated law | of density for the earth's interior  $(\sin nr/r)$ , which Laplace suggested as a consequence of supposing the earth to be a liquid globe, having pressure increasing from the surface inwards in proportion to the augmentation of the square of the density. With Ritter, however, the value of n is taken equal to  $\pi/R$ , so as to make the density zero at the bounding surface (r=R). With Laplace, n is taken equal to  $\frac{5}{6}\pi/R$  to fit terrestrial conditions, including a ratio of surface density to mean density which is approximately The ratio of surface density to mean density given by Laplace's law, with  $n = \frac{5}{6}\pi/R$ , is in fact 1/2.4225, which is as near to 1/2.5 as our imperfect knowledge of the surface density of the earth requires.

<sup>\*</sup> American Journal of Science, July 1870, p. 69. † See Appendix to the present paper, Tables I...IV.

<sup>†</sup> Wiedemann's Annalen, Bd. xi. 1880, p. 338. § Brit. Assoc. Report, 1883, p. 428.

Mécanique Celeste, vol. v. livre xi. p. 49.

§ 29. For the case  $\kappa = 5$ , Schuster found a solution in finite terms, which with our present notation may be written as follows:—

$$\frac{A}{S}\rho^{\frac{1}{6}} = t = \Theta_5(x) = \frac{x\sqrt{3}}{\sqrt{(3x^2 + 1)}} \quad . \quad . \quad (27).$$

This makes t=1 at the centre  $(\sigma/r=x=\infty)$ . At very great distances from the centre (x = 0) it makes

$$t = x \sqrt{3} = \frac{\sigma\sqrt{3}}{r}$$
, and  $\rho = \left(\frac{St}{A}\right)^5 = \left(\frac{S\sqrt{3}}{A}\right)^5 x^5 = \left(\frac{S\sqrt{3}}{A}\right)^5 \frac{\sigma^5}{r^5}$  (28).

Using (27) in (25), we find

$$\frac{m}{E} = \frac{(\kappa + 1)S\sigma}{e^2} \frac{\sqrt{3}}{(3x^2 + 1)^{3/2}} \cdot \dots (29);$$

and if in this we put x=0, we find

$$\frac{\mathbf{M}}{\mathbf{E}} = \frac{(\kappa + 1)\mathbf{S}\sigma\sqrt{3}}{e^2} \quad . \quad . \quad . \quad . \quad (30),$$

where M denotes the whole mass of the fluid. Thus we see that while the temperature and density both diminish to zero at infinite distance from the centre, the whole mass of the fluid is finite.

§ 30. It is both mathematically and physically very interesting to pursue our solutions beyond  $\kappa = 5$ , to larger and larger values of  $\kappa$  up to  $\kappa = \infty$ : though we shall see in § 43 below, that, for all values of  $\kappa$  greater than 3 (or  $k < 1\frac{1}{3}$ ), insufficiency of gravitational energy causes us to lose the practical possibility of a natural realization of the convective equilibrium on which we have been founding. But notwithstanding this large failure of the convective approximate equilibrium, we have a dynamical problem of true fluid equilibrium, continuous through the whole range of  $\kappa$  from -1 to  $-\infty$ , and from  $+\infty$  to 0; that is to say, for all values of k from 0 to  $\infty$ . In fact, looking back to the hydrostatic equation (10), and the physical equations (1), or (7), and (16), we have the whole foundations of equations (17) to (26), in which we may regard t merely as a convenient mathematical symbol defined by (6') in § 4. positive value of k is clearly admissible in (1), if we concern ourselves merely with a conceivable fluid having any law of relation between pressure and density which we please to give it, subject only to the condition that pressure is increased

by increase of density. It is interesting to us now to remark, what is mathematically proved in § 44 below, that unless  $k>1\frac{1}{3}$ , the repulsive quality in the fluid represented by k in equation (1) is not vigorous enough to give stable equilibrium to a very large globe of the fluid, in balancing the conglomerating effect of gravity.

§ 31. As to the range of cases in which  $\kappa$  has finite values greater than 5, we leave it for the present and pass on to  $\kappa = \infty$ , or k = 1. In this case equation (1) becomes

$$\frac{\rho}{\rho'} = \frac{p}{p'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (31);$$

which is simply Boyle's law of the "Spring of air," as he called it. It was on this law that Newton founded his calculation of the velocity of sound, and got a result that surprised him by being much too small. It was not till more than a hundred years later that the now well-known cause of the discrepance was discovered by Laplace, and a perfect agreement obtained between observation and dynamical theory. But at present we are only concerned with an ideal fluid which, irrespectively of temperature, exerts pressure in simple proportion to its density. This ideal fluid we shall call for brevity a Boylean gas.

§ 32. For this extreme case of  $\kappa = \infty$ , our differential equation (24) fails; but we deal with the failure by expressing t in terms of  $\rho$  by (19), and then modifying the result by putting  $\kappa = \infty$ . We thus find

$$\frac{d^2 \log \rho}{dx^2} = -\frac{\rho}{x^4}; \quad \text{where } x = \frac{\sigma}{r} \quad . \quad . \quad (32);$$

 $\sigma$  denoting a linear constant given by (37) below. Equation (32) is the equation of equilibrium of any quantity of Boylean gas, when contained within a fixed spherical shell, under the influence of its own gravity, but uninfluenced by the gravitational attraction of any matter external to it. The value of  $\sigma$  might, but not without considerable difficulty, be found from (22) by putting  $\kappa = \infty$ . But it is easier and more clear to work out afresh, as in § 33 below, the equation of equilibrium of a Boylean gas, unencumbered by the exuvize of the adiabatic principle from which our present problem emerges.

§ 33. Let 
$$p = B\rho$$
. . . . . . (33),

where B denotes what we may call the Boylean constant for

the particular gas considered; being its pressure at unit density. According to our units, as explained in §§ 10, 11, 12, B is a linear quantity. The analytical expression of the hydrostatic equilibrium is

where [(16) repeated]

$$g = \frac{m/r^2}{E/e^2} = \frac{3}{5 \cdot 6 \cdot e} \frac{\int_0^r dr \, r^2 \rho}{r^2} \quad . \quad . \quad . \quad (35).$$

Eliminating p from (34) by (33), and multiplying both members by  $r^2$ , we find

$$-r^{2}\frac{d\log\rho}{dr} = \frac{3}{5 \cdot 6.e.B} \int_{0}^{r} dr \, r^{2}\rho = \frac{e^{2}m}{BE} . \quad . \quad (36).$$

Differentiating this with reference to r, and then transforming from r to x as in equations (21) . . . . (24) above, we find (32), with the following expression for  $\sigma$ :—

$$\sigma^2 = \frac{5.6}{3} eB$$
 . . . . . . . (37).

The equation of the first and third members of (36) gives

$$\frac{m}{E} = \frac{B\sigma}{e^2} \frac{d\log\rho}{dx} \quad . \quad . \quad . \quad (38).$$

§ 34. Let now  $\rho = F(x)$  be any particular solution of (32); we find as a general solution with one disposable constant C,

$$\rho = \operatorname{CF}\left(\frac{x}{\sqrt{\operatorname{C}}}\right)$$
 . . . (39),

which we may immediately verify by substitution in (32) (compare § 25 above). The particular solution F must belong to one or other of the two classes, class A and class B, defined in § 25 above.

§ 35. We shall denote by  $\Psi(x)$  what F(x) of § 34 becomes, when the particular solution of (32), denoted by F, is of class A, with units so adjusted as to make  $\Psi(\infty) = 1$ ; that is to say, central density unity. Mr. Green in his Appendix

to the present paper has calculated  $\Psi(x)$  and  $\Psi'(x)/\Psi(x)$ , through the range from  $x=\infty$  to x=1. His results are shown in Table V. of the Appendix. Thus we may consider  $\Psi(x)$  and its differential coefficient  $\Psi'(x)$  as known for all values of x through that range.

§ 36. Using this solution,  $\Psi(x)$ , instead of F in (39) above, we find that the solution of class A, which makes the central density C, is

$$\rho = C\Psi\left(\frac{x}{\sqrt{C}}\right)^{\frac{1}{2}} \dots \dots (40)$$

and when we insert this expression for  $\rho$  in equation (38) we obtain

$$\frac{m}{E} = \frac{B\sigma}{e^2} \frac{1}{\sqrt{C}} \frac{\Psi'\left(\frac{x}{\sqrt{C}}\right)}{\Psi\left(\frac{x}{\sqrt{C}}\right)} \quad . \quad . \quad (41).$$

From equations (40) and (41), with values of  $\Psi\left(\frac{x}{\sqrt{C}}\right)$  and  $\Psi'\left(\frac{x}{\sqrt{C}}\right)/\Psi\left(\frac{x}{\sqrt{C}}\right)$  obtained from the curves of  $\Psi(x)$  and  $\Psi'(x)/\Psi(x)$  in the range from  $x=\infty$  to x=1, and with the relation  $r = \frac{\sigma}{x}$  where  $\sigma$  is given by (37) above, we can tell exactly the density at any point of a spherical mass of an ideal Boylean gas, and the mass of gas within each spherical surface of radius r, when the gas is in equilibrium under its own gravitation only, and has a density at its centre of any stated amount C. It is interesting to examine by means of these solutions the changes in  $\rho$  and m at any given distance from the centre when the central density C increases by any small amount dC; and to find also the changes in the radius of the spherical cell enclosing a given mass m, required to allow the mass to continue in equilibrium when the central density is increasing or diminishing continuously. The following table shows the values of  $\rho$  or  $C\Psi\left(\frac{x}{\sqrt{C}}\right)$ , and  $e^2m/EB\sigma$  or  $\Psi'\left(\frac{x}{\sqrt{C}}\right)/\sqrt{C}\Psi\left(\frac{x}{\sqrt{C}}\right)$ , for

several of the larger values of r, corresponding to the central densities 1 and 1.21 respectively.

§ 38. From this table we see that it is possible to have the same mass of an ideal Boylean gas  $(e^2m/EB\sigma = 21.9)$  distributed in two different equilibrium conditions within a given sphere  $(\sigma/r = 115)$ . We see also that in all smaller spheres the mass has increased, and in greater spheres it has decreased, through the alteration of density at the centre from 1 to 1.21. Indeed, when we trace the changes in the condition of any stated mass of a Boylean gas as its central density ideally increases from very small to very great values, we find that its radius diminishes till a certain central density has been reached, after which it increases till it becomes infinite.

§ 39. By taking any two values of C in equation (26) above, and comparing the two solutions thus obtained as in § 37, it may be verified that results similar to those found in the case of a finite mass of an ideal Boylean gas, are found also in the case of a finite mass of any gas for which  $\kappa>3$ , or  $k<1\frac{1}{3}$ ; while for any finite mass of a gas for which  $\kappa<3$ , an increase in the density at the centre is always accompanied by a decrease in the radius of the shell enclosing the mass in equilibrium. These differences in the

behaviour of the Boylean gas from that of gases for which  $\kappa < 3$ , and the resemblances of the Boylean gas and of gases for which  $\kappa > 3$  (of which it may be regarded as the limiting case,  $\kappa = \infty$ ), become of interest when we come to the question of the possibility of equilibrium of a mass of gas which is gradually losing energy by radiation into space. The result found above that there are two equilibrium conditions of a mass of any gas for which  $\kappa > 3$ , and one equilibrium condition of a mass of any gas for which  $\kappa < 3$ , within a given sphere, makes it desirable to investigate the nature of the equilibrium in each case, and leads us to the consideration of the energy required to maintain a mass of gas in equilibrium, within a sphere of radius R, in balancing the condensing influence of gravity.

§ 40. Let  $K_v$  denote the thermal capacity at constant volume of the particular gas considered. The energy within unit volume of the gas at temperature t is  $K_v \rho t$ ; and the total energy I, within a sphere of radius R, is given by

$$I = 4\pi K_v \int_0^R dr \, r^2 \rho t = K_v \int_0^R dm \, t$$
 . (42).

By using equation (6), and then integrating by parts, we obtain

$$\mathbf{I} = \frac{4\pi \mathbf{K}_{v}}{\mathbf{S}} \int_{0}^{\mathbf{R}} dr \, r^{2} p = \frac{4\pi \mathbf{K}_{v}}{\mathbf{S}} \left[ \left( \frac{1}{3} \, r^{3} p \right)_{0}^{\mathbf{R}} - \frac{1}{3} \int_{0}^{\mathbf{R}} dr \, r^{3} \frac{dp}{dr} \right] \quad \textbf{(43)} \; ;$$

and since p=0 at the outer boundary of the sphere and r=0 at the centre, we have

$$I = -\frac{4\pi K_v}{3S} \int_0^R dr \, r^3 \frac{dp}{dr} \quad . \quad . \quad (44)$$

Substituting now the expression given for  $-\frac{dp}{dr}$  in the equation of hydrostatic equilibrium (34), we obtain finally

$$I = \frac{4\pi K_v}{3S} \int_0^R dr \, r^3 g\rho \quad . \quad . \quad . \quad . \quad (45).$$

§ 41. The work which is done by the gravitational attraction of the matter within any layer of gas  $4\pi r^2 \rho dr$  in bringing that layer from an infinite distance to its final position in the sphere is given by

$$dw = 4\pi r^2 \rho \, dr \cdot gr \, . \, . \, . \, . \, . \, (46)$$
;

and the work done by gravity in collecting the whole sphere

of radius R is therefore

$$W = 4\pi \int_{0}^{R} dr \, r^{3} g \rho = \frac{e^{2}}{E} \int_{0}^{R} dm \, \frac{m}{r} \quad . \quad . \quad . \quad (47).$$

§ 42. From equations (45) and (47) we obtain, as the ratio of the intrinsic energy within the sphere of gas to the work done by gravity in collecting the whole mass from an infinite distance,

$$\frac{I}{W} = \frac{K_v}{3S} \quad . \quad . \quad . \quad . \quad (48)$$

If  $K_p$  be the specific heat of the gas at constant pressure, we have  $S = K_p - K_v$ , and equation (48) may now be written in the form

$$\frac{I}{W} = \frac{K_v}{3(K_p - K_v)} = \frac{1}{3(k-1)} = \frac{\kappa}{3} \quad . \quad . \quad (49).$$

§ 43. According to this theorem, it is convenient to divide gases into two species: species P, gases for which the ratio (k) of thermal capacity pressure constant to thermal capacity volume constant is greater than  $1\frac{1}{3}$ ; species Q, gases for which k is less than  $1\frac{1}{3}$ . And the theorem expressed mathematically in equations (48) and (49) may be stated thus:—"A spherical globe of gas, given in equilibrium, with any arbitrary distribution of temperature having isothermal surfaces spherical, has less heat if the gas is of species P, and more heat if of species Q, than the thermal equivalent of the work which would be done by the mutual gravitational attraction between all its parts, in ideal shrinkage from an infinitely rare distribution of the whole mass to the given condition of density"\*.

§ 44. It is easy to show from the theorem of §§ 42, 43 that the equilibrium of a globe of Q gas is essentially unstable. Let us first suppose for a moment that by a slight disturbance of the equilibrium condition the ratio I/W for the globe of Q gas becomes greater than that required for equilibrium by equation (49). Unless the excess of internal energy were quickly radiated away, the repulsive force which the globe of gas possesses by virtue of its internal energy would more than balance the condensing influence of gravity, and the globe would tend to expand. Since the internal energy lost in expansion is exactly equivalent to the work done against gravity, we see that the

<sup>\*</sup> Quoted from "On Homer Lane's Froblem of a Spherical Gaseous Nebula," 'Nature,' Feb. 14, 1907.

ratio I/W would continue to increase and the globe would become farther from an equilibrium condition than before. The expansion of the globe would therefore go on at an ever increasing speed till the density of the gas becomes infinitely

small throughout.

If, on the other hand, through a slight disturbance of the equilibrium condition, the ratio I/W becomes less than that required for equilibrium, the globe of gas would in this case tend to contract. The increase in the internal energy due to any slight condensation would be exactly equal to the thermal equivalent of the work done by gravitation; and the ratio I/W would therefore go on diminishing instead of increasing, as it would require to do if the gas is to be

restored to a condition of equilibrium.

§ 45. "From this we see that if a globe of gas Q is given in a state of equilibrium, with the requisite heat given to it no matter how, and left to itself in waveless quiescent ether, it would, through gradual loss of heat, immediately cease to be in equilibrium, and would begin to fall inwards towards its centre, until in the central regions it becomes so dense that it ceases to obey Boyle's Law; that is to say, ceases to be a gas. Then, notwithstanding the above theorem, it can come to approximate convective equilibrium as a cooling liquid globe surrounded by an atmosphere of its own vapour"\*.

 $\S$  46. But if, after being given in convective equilibrium as in  $\S$  45, heat be properly and sufficiently supplied to the globe of Q gas at its centre, the whole gaseous mass can be

kept in the condition of convective equilibrium.

§ 47. The theorem of §§ 42, 43 is given by Professor Perry on page 252 of 'Nature' for July 13, 1899; and in the short article "On Homer Lane's Problem of a Spherical Gaseous Nebula," published in 'Nature,' February 14, 1907, I have referred to it as Perry's theorem. Since this was written, however, I have found the same theorem given by A. Ritter on pp. 160–162 of Wiedemann's Annalen, Bd. 8, 1879, with the same conclusion from it as that stated in § 44 above, namely, that when  $k < 1\frac{1}{3}$  the equilibrium of the spherical gaseous mass is unstable.

§ 48. In the theorem of Ritter and of Perry, given in § 42, convective equilibrium is not assumed. For the purposes of our problem, indicated in § 21, it is desirable to obtain expressions for the energy and the gravitational work of a mass M in equilibrium with a stated density at its

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

centre, in terms of the notation of §§ 23...25 above. Thus, taking as our solution with central temperature C (equation 26),

$$t = C\Theta(z)$$
 . . . . (50),

where

$$z = x C^{-\frac{1}{2}(\kappa-1)}; \quad r = \sigma C^{-\frac{1}{2}(\kappa-1)}/z;$$

and where  $\sigma$  is given in terms of the Adiabatic Constant, A, by (22); we have from equations (25) and (50)

$$\frac{m}{E} = \frac{(\kappa + 1)S\sigma C^{-\frac{1}{2}(\kappa - 3)}}{e^2} \Theta'(z) \quad . \quad . \quad (51),$$

and by differentiating this we obtain-

$$\frac{dm}{E} = \frac{(\kappa + 1)S\sigma C^{-\frac{1}{2}(\kappa - 3)}}{e^2} \Theta''(z)dz \quad . \quad . \quad (52)$$

§ 49. With these values of t and dm substituted in the third member of equation (42), the expression for the internal energy, i, of the gas within a sphere of radius r becomes

$$i = \mathbf{K}_v \int_0^r dm \, t = -\frac{\mathbf{K}_v \mathbf{E}(\kappa + 1) \mathbf{S} \sigma \mathbf{C}^{-\frac{1}{2}(\kappa - 5)} \int_z^{\infty} dz \Theta''(z) \Theta(z)}{e^2}$$
(53).

By putting  $\Theta''(z) = - [\Theta(z)]^{\kappa}/z^4$  in this, and then integrating by parts as in § 40, equation (43), we may write i in the form—

$$i = \frac{K_v E(\kappa + 1) S \sigma C^{-\frac{1}{2}(\kappa - 5)}}{e^2} \left[ \frac{\left[\Theta(z)\right]^{\kappa + 1}}{3z^3} + \frac{\kappa + 1}{3} \int_z^{\infty} dz \frac{\left[\Theta(z)\right]^{\kappa}}{z^3} \Theta'(z) \right]$$
(54).

Similarly, from the third member of (47), with the values of m and dm given in (51) and (52) above, we obtain the following expression for the gravitational work, w, done in collecting the gas within a sphere of radius r from infinite space—

$$w = \frac{\mathbf{E}(\kappa+1)^2 \mathbf{S}^2 \sigma \mathbf{C}^{-\frac{1}{2}(\kappa-5)} \int_z^\infty dz \frac{[\Theta(z)]^{\kappa}}{z^3} \Theta'(z) \quad . \quad (55).$$

It is easy to verify from these equations for i and w that with  $S = K_p - K_v$ , as in § 42,

$$i = \frac{K_v E(\kappa + 1) S \sigma C^{-\frac{1}{2}(\kappa - 5)}}{e^2} \frac{[\Theta(z)]^{\kappa + 1}}{3z^3} + \frac{\kappa}{3} w . \quad (56) ;$$

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§ 50. For the complete mass of gas, M, which can be in convective equilibrium under the influence of its own gravitation only, with central temperature C, we have the following results:—

$$\frac{\mathbf{M}}{\mathbf{E}} = \frac{(\kappa + 1)\mathbf{S}\boldsymbol{\sigma}\mathbf{C}^{-\frac{1}{2}(\kappa - 3)}}{e^2}\boldsymbol{\Theta'}_{\kappa}(q) \quad . \quad . \quad . \quad . \quad (57) ;$$

$$R = \frac{\sigma C^{-\frac{1}{2}(\kappa-1)}}{q} \qquad . \qquad (58)$$

$$I = \frac{K_v E(\kappa + 1)^2 S \sigma C^{-\frac{1}{3}(\kappa - 5)}}{3 e^2} \int_q^{\infty} dz \frac{[\Theta(z)]^{\kappa}}{z^3} \Theta'(z) \quad (59) ;$$

$$\mathbf{W} = \frac{\mathbf{E}(\kappa+1)^2 \mathbf{S}^2 \boldsymbol{\sigma} \mathbf{C}^{-\frac{1}{2}(\kappa-5)} \int_a^{\infty} dz \frac{[\boldsymbol{\Theta}(z)]^{\kappa}}{z^3} \boldsymbol{\Theta}'(z) . \quad (60);$$

with

$$\sigma^2 = \frac{5 \cdot 6 \cdot e(\kappa + 1) A^{\kappa}}{3 \cdot S^{\kappa - 1}} \quad . \quad . \quad . \quad [(22) \text{ repeated}].$$

The two equations (59) and (60) give as before

§ 51. The equations of §§ 48...50, with equation (19), give the solution of Homer Lane's problem for all values of  $\kappa$  for which the function  $\Theta_{\kappa}(z)$  and its derivative  $\Theta'_{\kappa}(z)$  have been completely determined, namely for  $\kappa=1$  and  $\kappa=5$ , referred to in §§ 28, 29 above, and for the values 1.5, 2.5, 3, 4, for which the Homer Lane functions and their derivatives are given in the Appendix to the present paper (Tables I....IV.). It is important to remark that these equations indicate clearly the critical case  $\kappa=3$ , and that they also reveal some interesting peculiarities of the case  $\kappa=5$ ; which we have found to be the smallest value of  $\kappa$  for which a finite mass of gas is unable to arrange itself in equilibrium within a finite boundary (see §§ 27, 29).

Equation (57) shows that in spherical nebulas for whose gaseous stuff  $\kappa=3$  the total mass of any gas which can exist in the equilibrium condition corresponding to a definite central temperature, when so distributed throughout its whole volume that the temperature and density at every point are related to each other in accordance with a chosen value of the adiabatic constant A, can also be brought into the equilibrium condition corresponding to any smaller central temperature, through gradual loss of energy, without

disturbing the relation of temperature and density at any

point of the mass.

Equations (59) and (60) show that in spherical gaseous nebulas for whose gaseous stuff  $\kappa=5$  the total internal energy, and the gravitational work, corresponding to each equilibrium distribution of gas, has the same value, whatever be the central temperature or total mass, provided temperature and density at each point within the mass are related to each other in accordance with the same value of the adiabatic constant in each case.

[To be continued.]

LXIV. Laterally loaded Struts and Tie-rods. By Arthur Morley, M.Sc., Professor of Mechanical Engineering at University College, Nottingham \*.

THE frequent occurrence of laterally loaded struts and ties in structures and machines makes the subject one of some importance. Every horizontal strut or tie-rod carries a lateral load in its own weight, every vertical stanchion which carries a horizontal wind load, every beam which is not horizontal, and the coupling-rods of locomotives loaded transversely by their own centrifugal force, are common examples. The increase in the maximum intensity of stress due to a small transverse load on a strut which has a considerable axial thrust is very marked in long struts.

Prof. Perry † has given a method of finding the stresses in such cases, his solution embracing conditions of the most

general kind.

Three methods are in common use for the determination of the maximum intensity of stress in such cases. In each of these the resultant intensity of stress is found by taking the algebraic sum of that due to the axial thrust or pull and the intensity of bending stress. The methods differ in the calculation of the bending stress only; the usual assumptions are made and the simple Bernoulli-Euler theory employed; but the calculation of the maximum bending moment differs in the three methods as follows:—

(a) The maximum bending moment is taken as that due to the transverse loads only. This will evidently be nearly correct in a very short stiff beam having a small thrust or pull.

(b) To the bending moment which the lateral loads would

<sup>\*</sup> Communicated by the Author.

<sup>†</sup> Phil. Mag. March 1892.

alone produce is added that which would be caused by the axial load if the deflexions of the beam were due to the transverse loads only and were unaffected by the axial loads. This is the method usually given in the text-books for other

than very short beams.

(c) The bending moment resulting from the axial loads is estimated by means of the deflexions calculated from the axial and lateral loads jointly, and is added to that resulting from the lateral loads. This is the method adopted in the paper mentioned above; but in the common case chosen for illustration an approximation is made in estimating the deflexion.

# Object of this Paper.

The present paper is mainly concerned with the simple but most important cases of uniformly distributed and single concentrated loads and simple conditions of end support; its main object is to record the more exact solutions and to examine under what circumstances the simpler methods of calculation are approximately correct and to indicate the degree of approximation.

#### Notation.

The axis of x is taken through the centres of area of the two ends of the bar and the origin is midway between these points. The length of the strut or tie-rod in all cases is taken as l. The axial force is +P a thrust in the case of a strut, and -P a pull in the case of a tie-rod. The radius of gyration of the area of cross section A about a central axis perpendicular to the plane of bending is k, and the moment of inertia,  $k^2A$ , of the area A about the same axis is I. Only sections symmetrical about this axis are considered and the depth of section is taken as d. The average intensity of stress over the section is  $p_0 = \pm \frac{P}{A}$ .

Since the curvature is always small within the limits of elasticity, it is taken as  $\frac{d^3y}{dx^2}$ , and the bending moment, reckoned negative when it tends to bend the bar concave towards its undeflected position, is equal to  $\mathrm{EI}\frac{d^2y}{dx^2}$ , where E is the modulus of direct elasticity.

Case I.

Uniform straight strut with uniformly distributed load w per unit length, and ends freely hinged.

$$EI\frac{d^{2}y}{dx^{2}} = -\frac{w}{2} \left( \frac{l^{2}}{4} - x^{2} \right) - Py, \quad . \quad . \quad (1)$$

$$\frac{d^2y}{dx^2} + \frac{P}{EI}y = -\frac{w}{2EI} \left(\frac{l^2}{4} - x^2\right). \quad . \tag{2}$$

The conditions being y=0 for  $x=\frac{l}{2}$  and  $\frac{dy}{dx}=0$  for x=0, the solution is

$$y = \frac{w}{2P}x^2 - \frac{wl^2}{8P} - \frac{wEI}{P^2} \left(1 - \sec\frac{l}{2} \sqrt{\frac{P}{EI}} \cos\sqrt{\frac{P}{EI}}x\right), (3)$$

and at the origin

breadth.

$$y_0 = -\frac{wl^2}{8\overline{P}} - \frac{wEI}{\overline{P}^2} \left(1 - \sec\frac{l}{2}\sqrt{\frac{\overline{P}}{EI}}\right), \quad . \quad . \quad (4)$$

and the bending moment with sign reversed is

$$\mathbf{M}_0 = \mathbf{P} y_0 + \frac{1}{8} w l^2 = \frac{w \mathbf{E} \mathbf{I}}{\mathbf{P}} \left( 1 - \sec \frac{l}{2} \sqrt{\frac{\mathbf{P}}{\mathbf{E} \mathbf{I}}} \right), \quad . \quad (5)$$

or 
$$M_0 = \frac{wEI}{P} \left( \sec \frac{\pi}{2} \sqrt{\frac{P}{P_e}} - 1 \right)$$
, . . . . (6)

where  $P_e$  is Euler's limiting value of P for the ideal strut, in this case  $\frac{\pi^2 EI}{l^2}$ , which value makes M and y infinite.

The actual working value of  $\frac{P}{P_e}$  will rarely reach as much as  $\frac{1}{4}$  when there is no lateral load, and with a lateral load  $\frac{1}{5}$  may be taken as an extreme value. As the resistance to bending under end thrust alone in a plane perpendicular to that of the lateral loads will often be less than that to bending under end thrust in the plane of the lateral loads,  $\frac{P}{P_e}$  will often be much less than  $\frac{1}{5}$ , as for example in a rectangular section the depth of which is considerably greater than the

Applying the expansion

$$\sec \theta - 1 = \frac{\theta^2}{2!} + \frac{5\theta^4}{4!} + \frac{61\theta^6}{6!} + \frac{1385\theta^8}{8!} + \dots &c. to (6),$$

$$\mathbf{M}_{0} = \frac{wl^{2}}{8} \left\{ 1 + \frac{5\pi^{2}}{48} \frac{\mathbf{P}}{\mathbf{P}_{e}} + \frac{61\pi^{4}}{5760} \left(\frac{\mathbf{P}}{\mathbf{P}_{e}}\right)^{2} + \frac{277\pi^{6}}{258048} \left(\frac{\mathbf{P}}{\mathbf{P}_{e}}\right)^{3} + \dots &c. \right\} . (7)$$

the coefficients of the various powers of  $\frac{P}{P_e}$  differing but little from unity. This or (5) may also be written

$$\mathbf{M}_{0} = \frac{wl^{2}}{8} + \frac{5}{384} \frac{wl^{4}}{\text{EI}} \cdot \mathbf{P} \left\{ 1 + \frac{61\pi^{2}}{600} \cdot \frac{\mathbf{P}}{\mathbf{P}_{e}} + \frac{277\pi^{4}}{26880} \left(\frac{\mathbf{P}}{\mathbf{P}_{e}}\right)^{2} + \dots \&c. \right\}. (8)$$

The form (8) shows in a striking manner the relation of the approximate method (b) to the correct method of calculating the bending stress and the order of the error involved in the former; the first two terms of (8) represent the maximum bending moment as estimated by method (b), and the coefficients of the powers of  $\frac{P}{P_e}$  are nearly unity; also the first term of (7) or (8) represents the maximum bending moment as estimated in the method (a).

The equal-and opposite intensities of maximum bending stress in a symmetrical section are

$$p_b = \pm \frac{M_0}{Z} = \pm \frac{w E d}{2p_0 A} \left( \sec \frac{l}{2k} \sqrt{\frac{p_0}{E}} - 1 \right),$$

where  $Z = \frac{2I}{d}$  is the modulus of section.

The maximum intensity of the compressive stress is

$$f_c = p_b + p_0 = \frac{w E d}{2p_0 A} \left( \sec \frac{l}{2k} \sqrt{\frac{p_0}{E}} - 1 \right) + p_0,$$

and the maximum intensity of the tensile stress is

$$f_t = p_b - p_0 = \frac{w E d}{2p_0 A} \left( \sec \frac{l}{2k} \sqrt{\frac{p_0}{E}} - 1 \right) - p_0,$$

which may be positive or negative.

If  $\frac{P}{P_e} = \frac{1}{5}$  the error involved in calculating the bending stress intensities by method (a) is 20 per cent., and by method (b) 4 per cent.; practically the same proportions it may be noticed in either case that the first neglected term in the

series bears to the first term. The errors involved in calculating  $f_c$  the maximum intensity of stress due to the axial and lateral forces combined will be less than these amounts, the error depending on the amount of the lateral compared with the axial load, and the shape of cross section. Similarly the error in calculating  $f_t$  will be greater than the above amounts.

Prof. Perry's approximation mentioned above consists in substituting  $\frac{wl^2}{8}\cos\frac{x}{l}\pi$  for  $\frac{w}{2}(\frac{l^2}{4}-x^2)$  in (1), which is equivalent to substituting a smaller but not a uniformly distributed load  $\frac{\pi}{4}wl$  for the actual lateral load wl. This gives

$$y_0 = \frac{wl^2}{8(P_e - P)}$$
 and  $M_0 = \frac{1}{8}wl^2 \cdot \frac{P_e}{P_e - P}$ ,

the deflexion being rather below the true value for all values of P. The most serious error arising from this approximation is that in calculating the bending stress for high ratios of  $\frac{P}{P_e}$  assuming the limits of elasticity not to be exceeded. For  $\frac{P}{P_e} = 0.9$  the error is  $3\frac{1}{2}$  per cent. on the deflexion and somewhat less on the bending stress; that on the maximum tensile stress  $f_t$  is proportionally more than that on the bending stress.

#### Case II.

Uniform straight strut with central lateral load W and ends freely hinged.

The equation in this case is

$$\frac{d^2y}{dx^2} + \frac{P}{EI} \cdot y = -\frac{W}{2EI} \left(\frac{l}{2} - x\right), \quad . \quad . \quad (9)$$

and the conditions being as before,

$$y_0 = \frac{W}{2P} \sqrt{\frac{EI}{P}} \tan \frac{l}{2} \sqrt{\frac{P}{EI}} - \frac{Wl}{4P}, \quad . \quad . \quad (10)$$

and at the centre

$$-\mathbf{M}_{0} = \frac{\mathbf{W}}{2} \sqrt{\frac{\overline{\mathbf{E}}}{\overline{\mathbf{P}}}} \tan \frac{l}{2} \sqrt{\frac{\overline{\mathbf{P}}}{\overline{\mathbf{E}}\overline{\mathbf{I}}'}}......(11)$$

 $M_0$  and  $y_0$  being evidently infinite for  $P = \frac{\pi^2 EI}{l^2} = P_e$ .

Using the expansion

$$\tan \theta = \theta + \frac{1}{3}\theta^3 + \frac{2}{15}\theta^5 + \frac{17}{315}\theta^7 + \dots$$

or 
$$-M_0 = \frac{Wl}{4} \left\{ 1 + \frac{\pi^2}{12} \frac{P}{P_e} + \frac{\pi^4}{120} \left( \frac{P}{P_e} \right)^2 + \frac{17\pi^6}{20160} \left( \frac{P}{P_e} \right)^3 + \dots \&c. \right\},$$
 (12)

$$-\mathbf{M}_{0} = \frac{\mathbf{W}l}{4} + \frac{\mathbf{W}l^{3}}{48\mathbf{E}\mathbf{I}} \cdot \mathbf{P} \left\{ 1 + \frac{\pi^{2}}{10} \frac{\mathbf{P}}{\mathbf{P}} + \frac{17\pi^{2}}{1680} \left(\frac{\mathbf{P}}{\mathbf{P}}\right)^{2} + \dots \&c. \right\}, \quad (13)$$

which very clearly shows the relation of the calculation by the method (b) to the true bending moment. For  $\frac{P}{P_e} = \frac{1}{5}$  the error is under 4 per cent.

### Case III.

Uniform straight strut with uniformly distributed load w per unit length and ends fixed in the direction of the axis of x.

The equation is

$$\frac{d^2y}{dx^2} + \frac{P}{EI} \cdot y = -\frac{w}{2EI} \left( \frac{l^2}{4} - x^2 \right) + \frac{M_1}{EI}, \quad . \quad . \quad (14)$$

where  $M_1$  is the bending moment at the ends. The conditions being  $\frac{dy}{dx} = 0$  for x = 0, y = 0 for  $x = \frac{l}{2}$ , and  $\frac{dy}{dx} = 0$  for  $x = \frac{l}{2}$  the solution

$$y = \frac{w}{2P} \left\{ x^2 - \frac{l^2}{4} + l \sqrt{\frac{EI}{P}} \operatorname{cosec} \frac{l}{2} \sqrt{\frac{P}{EI}} \left( \cos \sqrt{\frac{P}{EI}} x - \cos \frac{l}{2} \sqrt{\frac{P}{EI}} \right) \right\}$$

 $\mathbf{gives}$ 

$$\operatorname{EI} \frac{d^2 y}{dx^2} = \frac{w \operatorname{EI}}{\operatorname{P}} - \frac{w l}{2} \sqrt{\frac{\operatorname{EI}}{\operatorname{P}}} \operatorname{cosec} \sqrt{\frac{\operatorname{P}}{\operatorname{EI}}} \frac{l}{2} \cos \sqrt{\frac{\operatorname{P}}{\operatorname{EI}}} \cdot x. \quad (15)$$

The points of inflexion are at a distance from the centre given by

$$x = \sqrt{\frac{\overline{EI}}{\overline{P}}} \cos^{-1} \left\{ \sqrt{\frac{\overline{EI}}{\overline{P}}} \cdot \frac{2}{l} \sin \frac{l}{2} \sqrt{\frac{\overline{P}}{\overline{EI}}} \right\},\,$$

which varies from  $\frac{l}{2\sqrt{3}}$  when P=0 to  $\frac{l}{4}$  when  $P=P_e=\frac{4\pi^2EI}{l^2}$ . Euler's limiting value for the ideal strut fixed at both ends.

At the origin

$$-\mathbf{M_0} = \frac{w \, \mathbf{EI}}{\mathbf{P}} - \frac{wl}{2} \sqrt{\frac{\mathbf{EI}}{\mathbf{P}}} \operatorname{cosec} \frac{l}{2} \sqrt{\frac{\mathbf{P}}{\mathbf{EI}}}, \quad . \quad (16)$$

and the bending moment of greatest magnitude is at the fixed ends where

$$M_1 = \frac{wEI}{P} - \frac{wl}{2} \sqrt{\frac{EI}{P}} \cot \frac{l}{2} \sqrt{\frac{P}{EI}}. \quad (17)$$

If the forms (16) and (17) are expanded they show a similar relation to those in cases I. and II. between the exact method of calculating the bending moment and method (b) if deflexions above or below the points of inflexion are used. These points as mentioned above vary somewhat in position according to the value of P and method (b) becomes less simple than the exact method.

#### Case IV.

Uniform straight strut with central load W and ends firmly fixed in the direction of the axis of x.

The equation is

$$\frac{d^2y}{dx^2} + \frac{P}{EI}y = -\frac{W}{2EI}\left(\frac{l}{2} - x\right) + \frac{M_1}{EI}, \quad . \quad (18)$$

where  $M_1$  is the bending moment at the fixed ends. The solution gives the bending moment with sign reversed,

$$\mathbf{M} = \frac{\mathbf{W}}{2} \sqrt{\frac{\mathbf{EI}}{\mathbf{P}}} \left\{ \tan \frac{l}{4} \sqrt{\frac{\mathbf{P}}{\mathbf{EI}}} \cos \sqrt{\frac{\mathbf{P}}{\mathbf{EI}}} x - \sin \sqrt{\frac{\mathbf{P}}{\mathbf{EI}}} . x \right\}, (19)$$

which vanishes for all values of P when  $x = \frac{l}{4}$ .

$$M_0 = \frac{W}{2} \sqrt{\frac{EI}{P}} \tan \frac{l}{4} \sqrt{\frac{P}{EI}} = -M_1$$
, . (20)

which becomes infinite for  $P = \frac{4\pi^2 EI}{l^2}$ .

And expanding (20),

$$\mathbf{M}_{0}\!=\!-\mathbf{M}_{1}\!=\!\frac{\mathbf{W}l}{8}+\frac{\mathbf{W}l^{8}}{384\mathrm{E1}}\,\mathbf{P}\left\{\,1+\frac{4\pi^{2}}{40}\!\left(\!\frac{\mathbf{P}}{\mathbf{P}_{e}}\!\right)\!+\!\frac{17\pi^{4}}{1680}\!\left(\!\frac{\mathbf{P}}{\mathbf{P}_{e}}\!\right)^{\!2}\!+\!\ldots\&c.\right\},(21)$$

where  $P_e = \frac{4\pi^2 EI}{l^2}$ , Euler's limiting value of P for the ideal strut.

This again shows the relation of the method (b) to the more exact method, the deflexions being reckoned above or below

the points of inflexion which are at  $x = \pm \frac{l}{4}$ . The coefficients of powers of  $\frac{P}{P_e}$  are nearly unity, and with any assigned ratio  $\frac{P}{P_e}$  the error is easily estimated and with usual working ratios will be very small.

Case V.

Uniform straight tie-rod with uniformly distributed load w per unit length and ends freely hinged.

This is the same as case I. with the sign of P reversed. The

solution of the equation is

$$y = -\frac{w}{2P}x^2 + \frac{wl^2}{8P} - \frac{wEI}{P^2} \left(1 - \operatorname{sech} \frac{l}{2} \sqrt{\frac{P}{EI}} \operatorname{cosh} \sqrt{\frac{P}{EI}} x\right), \quad (22)$$

and at the origin-

$$y_0 = \frac{wl^2}{8P} + \frac{wEI}{P^2} \left( \operatorname{sech} \frac{l}{2} \sqrt{\frac{P}{EI}} - 1 \right) \quad . \quad . \quad . \quad . \quad . \quad (23)$$

and at the origin the bending moment with sign reversed,

$$\mathbf{M_0} = \frac{wl^2}{8} - \mathbf{P}y_0 = \frac{w\mathbf{EI}}{\mathbf{P}} \left( 1 - \operatorname{sech} \frac{\mathbf{P}}{2} \sqrt{\frac{\mathbf{P}}{\mathbf{EI}}} \right), \text{ or } \frac{w\mathbf{EI}}{\mathbf{P}} \left( 1 - \operatorname{sech} \frac{\pi}{2} \sqrt{\frac{\mathbf{P}}{\mathbf{P}_e}} \right), \tag{24}$$

where  $P = \frac{\pi^2 EI}{l^2}$ .

And expanding (24),

$$M_0 = \frac{wl^2}{8} \left\{ 1 - \frac{5\pi^2}{48} \cdot \frac{P}{P_e} + \frac{61\pi^4}{5760} \left(\frac{P}{P_e}\right)^2 - \dots \&c. \right\}, \quad (25)$$

$$\mathbf{M_0} = \frac{w l^2}{8} - \frac{5}{384} \frac{w l^4}{\mathrm{EI}} \mathbf{P} \left\{ 1 - \frac{61\pi^2}{600} \left( \frac{\mathbf{P}}{\mathbf{P}_e} \right) + \frac{277\pi^4}{26880} \left( \frac{\mathbf{P}}{\mathbf{P}_e} \right)^2 - \dots &c. \right\}. \tag{26}$$

The errors involved in the use of the method (b) are here about the same as in case I. when  $\frac{P}{P_e}$  is small, a condition which would not be fulfilled in a tie-bar carrying a reasonable pull unless l is small or the lateral load is great. For tie-bars of considerable length (say l greater than  $20\,d$  for circular sections)  $\frac{P}{P_e}$  is generally greater than unity, and method (b) is no longer of any use when the lateral load is only the weight of the bar; but, on the other hand, the bending stresses are then small compared with the tension resulting from the axial pull P.

Prof. Perry's approximation gives

$$y_0 = \frac{wl^2}{8(P_e + P)}$$
 and  $M_0 = \frac{wl^2}{8} \cdot \frac{P_e}{P_e + P}$ .

For P=0 this underestimates the deflexion by  $2\frac{1}{2}$  per cent. but gives the correct bending moment; for other values of P it overestimates the value of the bending moment by a proportion which increases as P is increased; e. g., if P=P<sub>e</sub> the error is 2.6 per cent., and if  $\frac{P}{P_e} = 9$ , a very possible value in a tie-rod of circular section, the error is over 12 per cent. If l is increased indefinitely  $M_0$  according to this approximation approaches the limit  $\frac{\pi^2}{8} \frac{wEI}{P}$  instead of  $\frac{wEI}{P}$ , as in (24), a limit of error of 23 per cent. on the bending moment. But in cases where l is great the stress arising from the bending moment is usually unimportant compared with the axial tension, w being small.

The intensity of bending stress

$$p_b = \pm \frac{M_0}{Z} = \pm \frac{wEd}{2p_0A} \left( 1 - \operatorname{sech} \frac{l}{2k} \sqrt{\frac{p_0}{E}} \right). \quad . \quad (27)$$

The maximum intensity of tensile stress is

$$f_t = p_b + p_0 = \frac{w \to d}{2p_0 A} \left( 1 - \operatorname{sech} \frac{l}{2k} \sqrt{\frac{p_0}{E}} \right) + p_0;$$
 (28)

and the maximum intensity of compressive stress is

$$f_c = p_b - p_0 = \frac{w E d}{2p_0 A} \left( 1 - \operatorname{sech} \frac{l}{2k} \sqrt{\frac{p_0}{E}} \right) - p_0, \quad . \quad (29)$$

which when negative gives the minimum intensity of tensile stress.

The pull  $p_0$  per unit area of cross section which with given load and dimensions makes  $f_t$  a minimum may be found from (28), and the value of  $p_0$  which makes  $f_c$  zero may be found from (29).

### Case VI.

Uniform straight tie-rod with central load W and ends freely hinged.

The equation is

$$\frac{d^2y}{dx^2} - \frac{\mathbf{P}}{\mathbf{E}\mathbf{I}} \cdot y = -\frac{\mathbf{W}}{2\mathbf{E}\mathbf{I}} \left(\frac{l}{2} - x\right). \quad . \quad . \quad (30)$$

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The conditions being as in cases I., II., and V.,

$$y_0 = \frac{Wl}{4P} - \frac{W}{2P} \sqrt{\frac{\overline{EI}}{P}} \tanh \frac{l}{2} \sqrt{\frac{\overline{P}}{\overline{EI}}}, \quad (31)$$

and the central bending moment

$$-M_0 = \frac{W}{2} \sqrt{\frac{\overline{EI}}{\overline{P}}} \tanh \frac{l}{2} \sqrt{\frac{\overline{P}}{\overline{EI}}}; \quad . \quad . \quad (32)$$

and expanding this

$$\begin{split} -\,\mathrm{M}_0 &= \frac{\mathrm{W}\,l}{4} \left\{ 1 - \frac{\pi^2}{12} \! \left( \frac{\mathrm{P}}{\mathrm{P}_e} \right) + \frac{\pi^4}{120} \! \left( \frac{\mathrm{P}}{\mathrm{P}_e} \right)^{\!2} - \frac{17\pi^6}{20160} \! \left( \frac{\mathrm{P}}{\mathrm{P}_e} \right)^{\!3} + \ldots \&\mathrm{c.} \right\}, \, (33) \\ &\text{where } \mathrm{P}_e &= \frac{\pi^2 \mathrm{EI}}{l^2}, \end{split}$$

or

$$- M_0 = \frac{Wl}{4} - \frac{Wl^3}{48EI} P \left\{ 1 - \frac{\pi^2}{10} \left( \frac{P}{P_e} \right) + \frac{17\pi^4}{1680} \left( \frac{P}{P_e} \right)^2 - \dots &c. \right\}. \quad (34)$$

Here as in case V. for calculation of bending stresses method (b) is evidently a good approximation only when  $\frac{P}{P_e}$  is small, i. e. when the bar is short or the lateral load great: for  $\frac{P}{P_e} = \frac{1}{5}$  the error is 3 per cent.

Other cases with the same simple loadings as the above naturally suggest themselves, such for instance as those in which clamps fixing the ends at any assigned inclination to the axis of x increase or decrease the flexure due to the lateral and axial loads, and those in which the longitudinal loads not passing through the centres of area of the ends of the strut or tie-rod may increase or decrease by their eccentricity the deflexion and bending moment resulting from the lateral loads.

LXV. The Changes in Velocity, in an Electric Field, of the  $\alpha$ ,  $\beta$  and Secondary Rays from Radioactive Substances. By A. S. Eve, M.A., Assistant Professor of Mathematics, and Lecturer in Radioactivity, McGill University, Montreal\*.

IN a paper on Secondary Radiation communicated to this Magazine in December 1904, it was stated by me that the secondary rays from substances, due to the  $\beta$  and  $\gamma$  rays of radium, were homogeneous in character, and on that

<sup>\*</sup> Communicated by the Author.

supposition values of the coefficients of absorption by aluminium were given for various radiators. It has since been shown by S. J. Allen\*, and others, that the secondary electrons really move with velocities as widely different as those of the  $\beta$  rays themselves. The mistake in my paper arose partly from working with too thick an aluminium face to the electroscope, and from using too light a substance, namely paper, as radiator. Allen also proved that the secondary radiations from lead or zinc had penetrating powers and, therefore, velocities almost as great as those of the particles from radium C; but that is not the case for light substances such as wood, paper, aluminium or paraffin.

It seems desirable in the first place to give corrected values † for the coefficients of absorption by aluminium in the case of some different secondary radiating substances, because these results have considerable bearing on the subsequent and main

work described in this communication.

The values of  $\lambda$  for secondary rays have been determined

in the following manner:-

About fourteen milligrams of pure radium bromide were placed in two sealed glass test-tubes. The primary  $\beta$  and y rays struck the radiating plates, which were several centimetres thick, and had an area of 22 × 22 square centimetres. The secondary incident rays were tested in a gold-leaf electroscope of small natural leak, measuring  $10 \times 10 \times 16$  c.c. One of the larger faces was removed, a few fine wires were stretched across, and the open side was then covered with thin aluminium leaf 0.00031 cm. thick. Rutherford has found that passage through such a sheet of aluminium reduces the length of the range in air of the a particle by 0.5 cm. only. certain, therefore, that such a layer of aluminium will scarcely affect the passage of  $\beta$  or of secondary rays. In front of the electroscope aluminium screens could be placed; both these and the electroscope were separated from the radium by 15 cms. thickness of lead. The coefficients of absorption were calculated in the ordinary way between the various thicknesses stated in the first column of Table I. In the first and second rows of figures the atomic weights and secondary radiation values are stated. In the second column are the values of  $\lambda$  for primary rays, and in the other columns the values for secondary rays from the various substances named.

\* Phys. Review, August 1906.

<sup>†</sup> Since this paper was forwarded for publication I have read a communication by H. Starke in *Le Radium* (Feb. 1908). He had obtained results with which those given in the first part of this paper are in general agreement.

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Table I. Values of  $\lambda$  for aluminium as absorber.  $\beta$  and  $\gamma$  rays.

	PRIMARY.	SECONDARY.			
Substance		Lead.	Iron.	Brick.	Carbon.
Atomic Weight		207	56	•••	12
$\left\{ egin{array}{ll} \operatorname{Secondary} \\ \operatorname{Radiation} \end{array} \right\}  \cdots$		106	72	48	36
Thickness in cms. Al.					
0009	48	48	71	-70	90
0 - 021	24	29	40	47	50
.021042	19	20	31	23	28
.042063	14	16	20	18	16
·063-·084	12	14		15	10
.084105	10	12		14	

These figures show that the secondary rays from lead are nearly similar to the primary rays from radium, as Allen proved. The rays from the lighter substances are more easily absorbed, especially at first. The lighter the substance, the less is the radiation, the less is the group velocity, and the

quicker the absorption by the screens.

It will be proved later by an electrical method that this is a case not of selective absorption, but of difference in velocity. The table shows also that the more penetrating rays from the various substances approximate in character to one another and to the primary rays. As the lighter substances emit electrons which, regarded as a group, have lower velocities than those from the heavier substances, we must conclude that the secondary rays are to a large extent intrinsic and projected from the radiating substance; they are not merely diffusely scattered primary rays. It may be remarked, however, that Allen has shown that the tertiary rays, from lead-lead-radium, are more easily absorbed than the secondary rays from lead. It is not difficult to arrange lead plates in such a way as to observe tertiary and even quaternary radiations. The relative amounts observed by me in one arrangement of apparatus were-

> Secondary ..... 70.5 divisions a minute, Tertiary ...... 6.7 ,, ,, Quaternary ... 0.5 ,, ,,

The values of  $\lambda$  are more difficult to determine, but using an aluminium screen 0.021 cm. thick, the values were about—

Primary	24
Secondary	
Tertiary	

It is strange that whilst secondary rays from lead are so like the primary rays which cause them, yet the tertiary should be different in absorbability from both. Judging from the curves published by Allen, the tertiary rays from lead are absorbed at the same rate as the secondary rays from paper, and my results seem to agree; for the tertiary from lead and the secondary from carbon have values for  $\lambda$  not far apart.

## Penetrating Secondary Rays.

If lead and brick are respectively examined as radiators, and their radiations are in turn cut off from the electroscope by a thick book, or by a sufficient thickness of aluminium, it will then be found that brick becomes a more efficient radiator than lead. If curves are plotted with the thickness of screens as abscissæ and the ionizations in the electroscope as ordinates, then the curves cross one another. The ionization values obtained in one experiment were:—

TABLE II.

Thickness of Aluminium Screens.	Lead.	Brick.
cm. 0	106	48
.04	37	15
.08	20	10
•16	8.3	7.9
.25	5.7	7.7
.50	4.3	6.9

The lead and brick radiators were both a little more than 5 cms. thick, and of nearly the same area. Again, using two stout books as screens (Drude's 'Optics' and Wood's 'Optics'), protected in all cases from the radium by 15 cms. of lead, the figures obtained were—

No radiator	4.1	divisions	a minute,
Lead radiator		22	,,
Brick radiator	6.8	22	22

Using another book as screen the values for the radiators named, for a different arrangement from the above, were—

Radiator.	Ionization.
None	 3.00
Lead	 3.44
Books	 4.15
Carbon	 4.50
T	 4 20
Cement	 . 4.80
$\operatorname{Brick}$	 

These results agree with the statement made in my first paper, that thick blocks of brick, slate, cement, granite, give rise to very penetrating rays. It can be proved that these rays come from considerable depths. With a book screen and carbon radiators the effects in divisions a minute were—

Carbon. No. of Radiating Plates.	Secondary Radiation.
0	3.00
1	3.48
2	4·00
3	4.52
3+a brick behin	d 4.68

Now these carbon plates were each 1.5 cm. thick.

Again, with wood or slate radiators, 0.75 and 0.5 cm. thick respectively, the measured movements of the gold-leaf were, when the screen was 4 sheets of aluminium each 0.04 cm. thick, as follows:—

	RADIATORS.			
No. of Sheets of:-	Wood (each 0.75 cm.).	Slate (each 0.5 cm.)		
1	6:42	6.96		
2	6.48	<b>7</b> ·68		
3	6.50	8:37		
4	•••	8.94		
5	6.70	_		
6		9.42		
7	6.85			
8	***	9.80		
9	6.97	**************************************		

Thus these penetrating rays came from a depth of about 6 cms. of wood or 4 cms. of slate. It is difficult to decide whether these rays are high velocity scattered primary  $\beta$  rays, or secondary negative rays, or secondary  $\gamma$  rays due to the primary  $\gamma$  rays, or secondary  $\gamma$  rays due to the expulsion of secondary  $\beta$  rays, or secondary  $\gamma$  rays due to the stopping of primary  $\beta$  rays. There is some evidence that they are secondary  $\gamma$  rays, but it is not conclusive. The paper by A. S. Mackenzie, in this Magazine, July 1907, shows that there are remarkable conditions, depending on direction, when  $\gamma$  rays traverse matter.

In the experiments made by Cooke on the penetrating radiation due to the earth, he found that brick gave rise to a very penetrating radiation. As clay generally contains radium it was natural to attribute the effect observed by Cooke to the presence of radium in the brick. It is probable, however, that the penetrating rays were due to the secondary radiation set up in the bricks by the radium and thorium in the ground, and not chiefly by the minute amount in the bricks employed. I have not succeeded in obtaining these penetrating rays from lead; they appear to arise in the lighter substances.

#### Electrical Method.

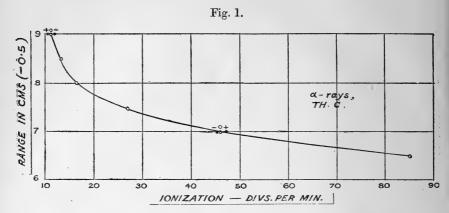
By an important experiment it was proved by Lenard\* that the cathode rays could be accelerated or retarded in an electric field, when the particles moved along the lines of force. He found that the value of e/m remained nearly constant, whilst the change in the velocity amounted to more than 20 per cent. for a difference of potential of 29,000 volts.

It seemed possible to apply a similar method to the  $\alpha$  and  $\beta$  rays from the radioactive substances, and to the secondary rays produced by the  $\beta$  and  $\gamma$  rays.

## a Rays.

A metal plate, 10 × 8 cms., was charged negatively and exposed to the emanation from thorium hydroxide until an active deposit of maximum activity was obtained. The plate was then placed parallel and opposite to the thin aluminium face of the gold-leaf electroscope, and was insulated on a block of paraffin so that it could be charged to about 30,000 volts, either positive or negative, by a Wimshurst influence-machine. One pole of the machine was earthed, a Leyden-jar was used to steady the potential of the other, and the potential, which

could be modified by a spark-gap, was measured by a Kelvin electrostatic voltmeter.



The range of the  $\alpha$  particle from Th C was found to be 8.5 cms. by Rutherford and Hahn; and the bend at 8 cms., shown in (fig. 1) is due to the entry of the  $\alpha$  rays into the electroscope at that range, for it is known that the aluminium face of the electroscope is equivalent to 0.5 cm. of air. The curve (fig. 1) is drawn with the ionization effects as abscissæ and the ranges as ordinates, following the well-known method of Bragg.

At 9 cm. no  $\alpha$  rays enter the electroscope, and a negative charge given to the active plate accelerates the  $\beta$  rays, and a positive charge retards them. Oblique rays are bent towards or from the electroscope according to the sign of the charge. The charge actually observed was 12 per cent. of the mean value, and the effect for negative was greater than the effect

for the positive charge.

At 7 cms. the  $\alpha$  rays were accelerated by a positive charge and retarded by a negative charge. The difference observed was 3 to 3.5 per cent. for potential-differences of  $\pm 30,000$  volts, and the effect for a positive charge was then greater. At 8 cms. no change could be observed because the acceleration of the  $\alpha$  rays balanced the retardation of the  $\beta$  rays, and conversely. Only the very ends of the ranges of the  $\alpha$  rays were inside the electroscope at this distance.

If the field were uniform the  $\alpha$  particles, projected in all directions, would describe parabolas, bent towards the electroscope for a positive charge, and away from the electroscope for a negative charge. For the  $\beta$  particles the reverse statement is true. The effect may be compared to the motion of

water issuing from a rose at the end of a hose directed to or from the earth.

It is easy to estimate the change of velocity for an a particle moving by any path from the plate at 30,000 volts to the electroscope at zero potential, for the change of kinetic energy is equal to the work done, so that

$$\frac{1}{2}mv^{2} - \frac{1}{2}mu^{2} = \pm eV,$$
or 
$$v^{2} = u^{2} \pm 2\frac{e}{m}V.$$

Here u is the velocity of projection, v of arrival, V is the potential-difference, e the ionic charge, and m the mass, expressed in E.M. units, and grams. The sign selected depends upon that of the charge. It has been proved by Rutherford and Hahn that for Th C,

$$u = 1.98 \times 19^9$$
,  $\frac{e}{m} = 5.6 \times 10^3$ , and  $V = 3 \times 10^{12}$ .

Hence

$$v^2 = (393 \pm 3.36)10^{16}$$
 and  $v = 19.91 \times 10^8$ , or  $19.74 \times 10^8$ ;

so that the total calculated difference per cent. for a change of sign of the potential is 0.8.

The effect of absorption by the air has not been considered. The change in ionization observed is not necessarily proportional to the change of velocity produced. The large change observed at 7 cms. (3 per cent.) was due in part to the bending of the rays, and to the consequent increased length of path, of the oblique rays, which is in the electroscope. Moreover, oblique rays which barely reach the electroscope when the plate is uncharged would be bent inside when the charge is given. The fact that no effect was observed at 8 cms. for a reversal of potential shows that the  $\alpha$  ray change then balanced the  $\beta$  ray change, and that the electric field altered the velocity of the normal  $\alpha$  rays, and that the actual range of the a particles was increased or decreased according to the direction of the lines of force. endeavoured, hitherto without success, to observe this change of range with a Crookes spinthariscope, using an ebonite cylinder; the eyepiece was earthed, and a wire, covered with radium C, was placed inside at the bottom on a plate raised to +30,000 volts. It is easy to show that the expected change of range must be small and difficult to detect, about 1.4 mm. for a reversal of potential \*.

<sup>\*</sup> Rutherford, Phil. Mag. Oct. 1906.

A Kelvin dynamo-static machine, kindly lent by Professor Owens, enabled me to work at a higher potential than with the Wimshurst machine. But sparks passed from the Th C plate and perforated the thin face of the electroscope, and ions then rushed inside. The holes could be repaired with very thin aluminium leaf, but observations were difficult to make.

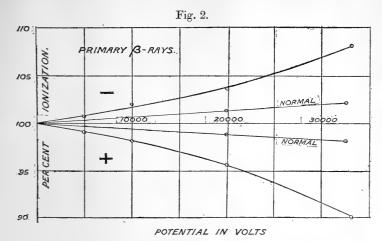
It may be here stated that it is important to have the mica windows of the electroscope as small as possible, otherwise the readings of the gold-leaf are not the same for positive and negative charges of the leaf, owing to induction effect, electric wind, &c. It is well to have a large well-earthed sheet of wide-meshed wire-netting just in front of the electroscope. This screens off the induction effect, and it does not interfere with the success of the experiment. The motion of the gold-leaf was remarkably steady and unaffected by the high potential in its neighbourhood.

This experiment with the  $\alpha$  rays shows in a simple manner the fact, proved by Rutherford, and later by Becquerel, that the  $\alpha$  particle carries a positive charge, and it indicates that the length of the range of these particles can be increased or decreased to a slight extent by an electric field with lines

of force in the direction of motion.

# β Rays.

Active matter containing radium, spread over a brass plate 10 cms. in diameter, was covered by just sufficient aluminium to absorb the  $\alpha$  rays, and to prevent the escape of emanation. This, made by Dr. Rümelin, serves as a convenient  $\beta$ -ray standard. The plate was placed in front of the electroscope, about 20 cms. from it, and it was charged to  $\pm 30,000$  volts. The total change in the ionization amounted to about 12 per cent. of the value when the plate was uncharged. A considerable part of this change is due to the bending of oblique rays, in or out of the electroscope according to the sign of the charge; secondary rays from brass must be present. Using the dynamo-static machine and obtaining a higher voltage, about +50,000, a difference of more than 15 per cent. was produced by a reversal of the electric field. As the potential is gradually increased from zero, the ionizations for positive and negative charges on the brass plate are not equidistant from the mean value (fig. 2). It appeared easier to retard and decrease the rays entering the electroscope than to accelerate and increase them. It is unfortunate that there is so little evidence as to the relationship between the magnitude of the velocity of electrons and the ionization produced by them. According to Townsend the ionization decreases as the velocity increases. Again, in the case of high velocity



electrons it is difficult to increase their speeds because, as Kaufmann and others have shown, there is an increase of mass as the velocity approaches that of light. There are then two reasons why the outer curves, shown in fig. 2, should not be symmetrical about the axis of x.

It is easy to calculate the velocity of the  $\beta$  particle on its arrival at the electroscope. As before, we write

$$v^2 = u^2 \pm 2 \frac{e}{m} V$$
.

But here we may take

$$\frac{e}{m} = 10^7 \text{ and } u = 2.6 \times 10^{10}.$$
Hence,
$$u^2 = 6.7 \times 10^{20} \text{ and } 2\frac{e}{m} \text{V} = 6 \times 10^{19},$$
so that
$$v^2 = (67 \pm 6)10^{19}$$

$$= 6.1, \text{ or } 7.3, \times 10^{20},$$
and
$$v = 2.46, \text{ or } 2.70, \times 10^{10}.$$

There is then a calculated difference equal to 9.2 per cent. of the mean value. But the difference produced in the velocity need not cause a proportional difference of ionization in the electroscope. The result calculated above is independent of the path of the electron. But if the number of electrons entering the electroscope varies for positive and

negative charges on the active plate, then the observed effect

will not correspond with that calculated.

In order to test this point experimentally, a capsule containing 1.5 mgs. of radium was placed so that the  $\beta$  rays passed through a small hole in a block of wood, and entered normally the centre of the face of the electroscope. The diameter of the hole was 1.5 cm., and the length of it was 10 cms. The block of wood was covered with thin aluminium foil, was insulated on a block of paraffin, and charged as previously described. The observed difference for positive and negative potentials was 6.3 per cent., or about two-thirds of the calculated value (inner curves, fig. 2). It must be borne in mind that the  $\beta$  rays of radium always include secondary rays, and that a group of  $\beta$  rays has a very wide range of velocity, from almost that of light to that of the slowest electrons produced by secondary, tertiary, or higher order radiation. The value for the velocity of projection of the  $\beta$  particles assumed in the above calculation was selected from Allen's paper\*, as being that derived under conditions most similar to those obtaining in my work.

In this case, as with the  $\alpha$  particle, no allowance has been made for the absorption and scattering by air between the plate and the electroscope. Under more rigorous experimental conditions, it is possible that this method might throw light on the ionizations produced for various velocities of the

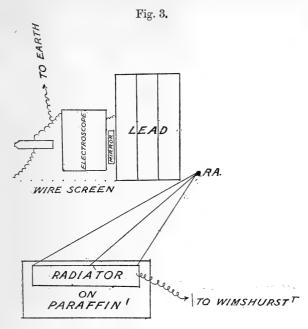
electrons.

### Secondary Rays.

The method described in this paper was next applied to the investigation of the nature of the secondary rays from various substances due to the  $\beta$  and  $\gamma$  rays from radium. About 14 mgs. of pure radium bromide were sealed in two thin glass test-tubes. The radiators were 5 cms. thick and measured  $22 \times 22$  cms. (fig. 3). They were insulated on blocks of paraffin and charged by the Wimshurst machine. A line from the radium to the centre of the radiating plate made an angle of 60° with the normal. When the radiator is charged to a high potential the primary rays will be repelled from, or attracted to, the radiator to an extent depending on the sign and the magnitude of the potential. This variation of the primary rays might have been avoided by using y rays only; but y rays are always accompanied by secondary rays from the screen which cuts off the  $\beta$  rays. Moreover, if all the radiators are of the same size and shape, and if they are placed in turn in the very same position, then, for any given

<sup>\*</sup> Phys. Review, Aug. 1906.

potential of whichever sign, the amount of primary  $\beta$  and  $\gamma$  rays falling on the plates will also be the same for all



substances used as radiators. Thus we have a thoroughly satisfactory comparative test of the secondary radiations from

the various materials employed.

The results obtained are shown in fig. 4 (p. 732), and it will be seen that the curves for each substance are unexpectedly symmetrical \*. The abscissæ denote potentials and the ordinates the percentage ionization effects observed. The upper curves were obtained when the radiators were negatively charged, and the lower curves for the reverse charge.

It will be noted that the lighter substances emit rays which, regarded as a group, have a relatively low velocity. These slow electrons are readily retarded and made to diverge when the radiator has a positive charge, and easily accelerated and concentrated by a repulsion towards the electroscope. The numerical values are given in Table III.,

p. 732.

<sup>\*</sup> The details of these curves (fig. 4) would repay further investigation. They diverge near the origin somewhat more rapidly than is shown in the figure, and there are some indications of points of inflexion on the upper curves. The details will necessarily depend on the angles and distances between the principal parts of the apparatus.

Fig. 4.

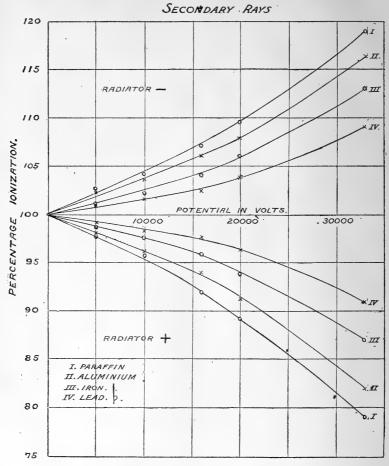


TABLE III.

				per cent. for	
Substance.	Density.	Secondary Radiation.	±34,000 volts.	±50,000 volts.	λ.
Lead	11.4	113	16.5	24	28.3
Iron	7.8	95	24.6	36	42.0
Aluminium	2.6	80	35.8	***	•••
Brick	2.2	79	34.0		50.0
Paraffin	0.9	65	41.0	48	

The third column gives the secondary radiation actually observed from the blocks used as radiators. The fourth column shows the differences per cent. on the mean value when the radiators were charged to 30,000 volts, first positive and then negative. In the fifth column are the differences per cent. for a higher potential, obtained with the dynamostatic machine. In the last column are the values of the coefficients of absorption by aluminium, 0.021 cm. thick, requoted from the first part of this paper. In this experiment the bricks were slightly moistened to make them conductors, and the paraffin was covered with aluminium foil, 00031 cm. thick. This thin layer of aluminium did not affect the radiation to a measurable extent, and it made the surface a conductor.

By a comparison of the fourth and fifth columns it appears that it becomes increasingly difficult, as the potential rises, to magnify the percentage differences for opposite charges of the radiator. The values of the coefficients of absorption in Table I. are also in accord with the view that together with the slower electrons, which form the bulk of the radiation from the lighter substances, there are also swifter electrons, which are with greater difficulty absorbed by matter or affected by an electric field.

These experiments as a whole indicate that the secondary rays from various substances have a distinctive group velocity depending on the density or atomic weight of the substance of the radiator. The values of the secondary radiation follow the order of the atomic weight, as shown by McClelland: it is now seen that the values of  $\lambda$  are also in inverse order of the secondary radiations, and that the percentage changes of ionization, due to the reversal of the electric field, are in that same inverse order.

Hence, secondary rays are in the main *intrinsic*, released from the atoms of the radiating substance, with distinctive group velocities depending on the density of the radiator. It appears that the secondary rays are for the most part not due to dispersed primary rays, which have entered the radiator, and by changes of path re-emerged; but it is not improbable that the secondary rays may include an unknown fraction of such primary rays. Thus  $\beta$  and  $\gamma$  rays appear merely to release the electrons, which issue from the radiators with velocities possibly depending on those which they had in the radiator \*.

<sup>\*</sup> Since writing the above I have received a paper by Bragg and Madsen (Trans of R. Soc. of S. Australia, 2 Jan. 1908; Phil. Mag. May 1908) advocating a different view.

If we take, for any radiating substance, the square root of the double ordinate, or percentage difference, at 20,000 or at 30,000 volts, and multiply by the actual secondary radiation from the plate, we get, with no great accuracy, a constant.

For example, with  $\pm 34,000$  volts:—

Substance.	Percentage Difference.	Square Root.	Secondary Radiation.	Product.
Carbon	35.6	5.96	69	410
Paraffin	41.0	6.40	65	415
Brick	34.0	5.84	79	470
Aluminium	35.8	5.98	80	476
Iron	24.6	4.96	95	470
Lead	16.5	4.06	113	460

This approximate rule emphasises the relationship between the velocity of the secondary rays and the amount of secondary radiation. The rule requires further investigation before it can be affirmed.

At some distance from the origin the curves shown on fig. 3 crudely resemble the parabola  $x^2 = ky$ , where k is a constant for each radiator. In the case of the less dense substances, it is found that when either the potential, or the distance between radiator and electroscope, is increased, there is not symmetry about the x axis, but the positive ordinates are numerically less than the negative ordinates for the same abscissæ. With a sufficiently high positive voltage the ionization could be reduced to zero, and a very large negative potential would cause each curve to approach an asymptote parallel to the x axis.

Some preliminary experiments were made to compare the quantity and quality of the secondary rays from hot iron plates and from hot bricks. The results were but slightly different, if at all, from those obtained from cold bricks and cold iron. Observations were made on radiators from a red-

heat to the temperature of the room.

It is usual to suppose that the secondary rays, which start from some depth within the radiator, must lose velocity on their passage through matter before they make their escape. The remarkable experiment of H. W. Schmidt \* throws doubt

<sup>\*</sup> Phys. Zeit. June 1, 1907.

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on this view. The result obtained by him was not for a wide range of thickness, amounting only to 0.5 mm. of aluminium, but within that limit he proved that the  $\beta$  rays from radium E continued to move with undiminished speed until they were actually absorbed. There is no doubt that after passage through matter the swifter electrons emerge, because the slower are first of all absorbed. The question remains an open one, whether the  $\beta$  particle loses velocity during its passage through a considerable thickness of matter. The question is always complicated by the attendant train of secondary rays which everywhere arise in the path of the particle through matter from the moment of its emission to the time of its complete absorption. In the case of the  $\alpha$  particle, Rutherford has clearly proved that velocity is lost during passage through matter.

In conclusion, one more experiment may be described. Fourteen milligrams of radium bromide were enclosed in a cylindrical block so that the  $\gamma$  rays passed through 2.5 cms. of lead before emerging to the air. The lead block was insulated, and placed before the electroscope. The potential was changed from + to -30,000 volts. The difference of the ionization observed was 3 per cent. of the mean value. The inner curves (fig. 2), otherwise obtained, almost represent the results of this experiment. The total ionization observed was mainly due to  $\gamma$  rays, and the change of ionization, on reversal of the sign of potential, was due to the electrons, which are projected from the surface of matter traversed by the  $\gamma$  rays\*.

This paper must be considered as preliminary, and there are some criticisms which may be applied to the method and to the arrangement of apparatus. Thus it is difficult to estimate the effect of the scattering and absorption by air of the rays employed, but it is not relatively large. Again, it might be expected that some of the ions generated outside the electroscope near the active plate would be accelerated in the electric field sufficiently to enter the electroscope. This either did not take place, or the effect was relatively too small to be noticed.

It is hoped that these experiments may be extended to other substances and that higher potentials will be employed. The electric method may throw some light on the ratio of the radiators exposed to primary Röntgen rays\*. The investigation of transmitted rays, and particularly of the rays from hot and cold bodies, should prove interesting when this method is applied.

Some of the work done overlaps that by Allen, with magnetic and electric deflexion methods. I trust that full justice has been done in making references to his valuable

paper.

#### Summary.

1. The coefficients of absorption by aluminium of the incident secondary radiations, due to the  $\beta$  and  $\gamma$  rays of radium, produced from various substances have been determined. The lighter substances emit negative rays not only less in quantity than the dense, but these rays are initially more readily absorbed. (Allen.)

2. Some substances, such as brick, slate, wood, paper, and carbon, give rise to penetrating incident secondary rays originating from several centimetres depth, which are either secondary  $\gamma$  rays or high velocity negative rays. After screening, the secondary radiation from brick or paper may

exceed that from a heavy substance, such as lead.

3. In an electric field, with the lines of force parallel to those of direction of motion, the velocity of the  $\alpha$  rays can be increased or diminished, and there is apparently a slight variation of range.

4. The same method may be applied to primary  $\beta$  rays or

to secondary rays due to  $\beta$  and  $\gamma$  rays.

- 5. The amount of secondary radiation is known to follow an order depending on the atomic weights of the radiators. It is shown by the method herein described that the velocities, regarded as a group, as well as the initial absorptions by aluminium, follow the same order, so that the main secondary negative rays are projected with velocities, which are a function of the density, or the atomic weight, of the radiating substance, the velocities being greater for the more dense. The main group of electrons therefore emerge with less velocity from the lighter substances.
- \* Recent experiments have been made, using the electric method described in this paper, with the secondary rays due to (1) X rays and (2)  $\gamma$  rays. In the case of X rays the cathode secondary rays are so rapidly absorbed by the air that they do not reach the electroscope. Hence a change from + to -50,000 volts in the potential of the secondary radiator made no difference in the ionization current. Perhaps there was a slight effect in the case of lead. The secondary rays, due to  $\gamma$  rays, gave percentage changes about equal to those observed in the secondary rays due to both  $\beta$  and  $\gamma$  rays of radium.

6. The square root of the percentage differences of ionization, due to a reversal of potential of the radiator, is inversely proportional to the secondary radiation from the radiator. This is a rough approximation for radiators of equal areas made of different substances.

McGill University, Montreal, February 1908.

# Note added 25th April, 1908.

In this paper I have upheld the old view that the secondary rays due to radium are not merely scattered primary. The experiments of H. W. Schmidt (Phys. Zeit. June 1, 1907) have to some extent weakened this theory. But the same observer has also shown that the  $\beta$  particle does not lose speed in passing through matter; and, if that is the case, the secondary electrons should have the same velocity as the primary; and they have not. Again,  $\gamma$  rays (we will suppose them to be æther pulses) give rise to secondary rays with velocities nearly equal to those of the secondary rays due to  $\beta$  particles. There seems no reason to suppose that the  $\beta$  rays could not cause the same projection of electrons from the atoms of the secondary radiator which we know that the  $\gamma$  rays cause. It is true that the view, advocated by Bragg, of the material nature of the  $\gamma$  rays is not out of harmony with observed facts; and, if that theory is correct, we may regard all secondary radiations, consisting of electrons with high velocities, as scattered primary rays.

LXVI. On the Electrical Charge of the Active Deposit of Actinium. By Sidney Russ, Demonstrator in Physics, Manchester University\*.

EXPERIMENTS by several observers have shown that the active deposit of Thorium is almost entirely directed to a negative electrode.

If into a vessel containing thorium emanation two wires be inserted, one charged negatively, the other positively, the amount of active deposit obtained on the negative wire is more than one hundred times that on the positive; this number, however, shows a considerable reduction if the pressure in the vessel is diminished to a few millimetres.

<sup>\*</sup> Communicated by Prof. E. Rutherford, F.R.S.

While working along similar lines with Actinium an exactly opposite effect was observed. Under the conditions of these experiments the activity of the negative was only twice that of the positive pole at atmospheric pressure, this ratio being *increased* to twenty-two on reducing the pressure

to a few millimetres. (Phil. Mag. May 1908.)

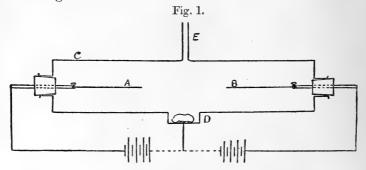
It was found, however, that by varying the experimental arrangements, the activity of the negative electrode could be made to vary from twice to more than a hundred times that of the positive electrode, without altering the pressure. It appears from the observations to be described, that the variable which determines the electrical charge of the carriers of the active matter, is the distance which they travel before reaching the electrode. If this distance be very small (a few millimetres) the particles are almost completely directed to the negative pole, the ratio mentioned above therefore being very large; as the distance of travel is increased this ratio shows a marked diminution.

The experiments indicate that the collisions of the active deposit particles with the gas molecules or ions with which they are mixed, determine the sign of the electrical charge

which they exhibit.

### Methods of Experiment.

The first experiments, which have already been partly described in the paper referred to above, were made in the following manner.



Two thin brass wires (A and B, fig. 1) 7.5 cms. long and .7 mm. diameter and 4 cms. apart, were made to lie along the axis of a brass tube C 30 cms. long and 4.2 cms. diameter. This tube was fitted with a small capsule D into which was placed a small quantity of a preparation of actinium.

The wire A was connected to the positive and B to the

negative pole of a battery of 320 volts, the brass tube being connected to the mid-point.

The exit-tube E could be connected to a Fleuss pump and a set of tubes containing calcium chloride and cotton-wool,

thus ensuring a supply of dry and dust-free air.

The wires were exposed usually for about two hours, when they were removed and their activities compared by measuring the saturation currents, which they separately produced in a cylinder connected to an electrometer.

Observations were made for pressures between 2 mms. and 76 cms. of mercury. The numerical results are collected in

Table I. and shown graphically in fig. 2.

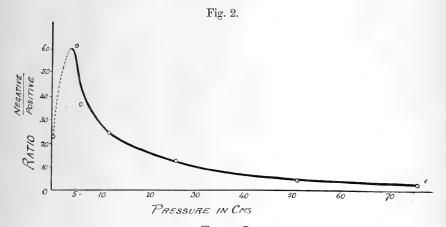


TABLE I.

Pressure	Activity in Un	Arbitrary its.	Ratio of Activities.
in cms.	Cathode.	Anode.	-ve +ve
76	15	7.5	2
51	35	8.7	4
26	62	5.2	12
12	137	5.7	24
6	200	5.5	36
5	270	4.5	60
-2	88	4.0	22

It will be observed that the *ratio* of the activities of the two wires increases steadily as the pressure is diminished,

attaining a maximum value at about 5 cms. pressure, then

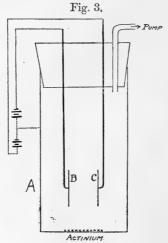
falling abruptly at a pressure of about 2 cm.

Owing to the very short life of the emanation from actinium (3.9 seconds) the distribution of the emanation in the cylinder C must be very different at the different pressures employed. At atmospheric pressure the emanation, owing to its rapid change into actinium A, will be confined to a comparatively small region round D, and the active deposit particles will have a greater distance to go before reaching the wires A and B than at the reduced pressures. It is probable that the decrease in the ratio of the activity of the cathode to that of the anode between pressures of 5 cms. and 2 mms. corresponds to the similar effect with thorium which has been already mentioned.

It is worth noting that the activity observed on the anode is almost entirely due to some of the active deposit particles being negatively charged. This was shown as follows:—An experiment was made in which no field existed between the wires and the containing cylinder, the activity observed on either of the wires was only about one-seventh part of that observed on the positive electrode. Hence the above conclusion.

At this stage it was resolved to vary the conditions of the experiment.

A preparation of actinium was placed at the bottom of a cylindrical vessel A (fig. 3) 9 cms. long and 4.5 cms. diameter,



which was closed by a rubber stopper through which passed two brass rods carrying two vertical brass plates B and C;

the brass plates, 1.5 cms. apart, were fixed parallel to one another and connected to the terminals of a battery as before; and their distance from the actinium could be varied as required.

Two series of observations were made, at 76 cm. and 2 mms. pressure, for different distances of the plates from the actinium. After an exposure of about two hours the plates were removed and their activities compared by means of an

a ray electroscope.

The numerical results are collected in Table II., and the variation with distance of the *ratio* of the activity of the negative to that of the positive plate is reproduced graphically in fig. 4 (p. 742).

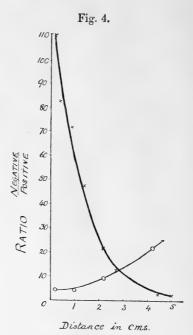
TABLE II.

		Activity in Ar	Ratio.	
	nce from	Negative plate. Positive plate.		- ve + ve
	76 cms.	Pressure.		
·2 cn	a	300	2.7	110
•4		250	3.0	83
.9		220	3.1	72
1.4		200	4.2	48
2.2		117	5.4	22
2.7		100	7.7	13
4.4		14	5.9	2.4
5.0	********	10	4:3	2.3
	2 mms.	Pressure.		
·2		7.9	1.6	4.9
1.0		7.4	1.5	4.8
2.2	•••••	14.1	1.3	9.6
4.2		22.0	1.0	22.0

An inspection of the second and third columns of Table II. shows that at 76 cms. pressure, whereas the active matter deposited on the negative plate *decreases* as the distance of the plate from the actinium is increased, the amount obtained on the positive plate *increases* till a distance 2.7 cms. from the

actinium is reached, after which a diminution occurs, probably owing to the fact that the total quantity of active matter collected on the two plates is then very small.

At 2 mms. pressure the active matter obtained on the negative plate shows an *increase* as the plate is removed from the actinium, while the quantity on the anode shows a steady decrease.



Crosses refer to 76 cms. pressure. Circles refer to 2 mms. pressure.

It will be seen from fig. 4 that at atmospheric pressure the negative plate is more than one hundred times as active as the positive for small distances from the actinium, a very large diminution in the ratio resulting as the distance is increased. The opposite effect holds at a pressure of 2 mms.

It has been shown by Debierne\* that the amount of emanation obtained from a uniform layer of actinium falls to half value on going 55 cm. from the layer. We should, therefore, expect a diminution in the activity of the plates as their distance from the actinium is increased; but the

RATIO of the activities on the two plates should remain the same. This is, however, far from being the case, and moreover the positive plate shows signs of increased activity as its distance from the layer of actinium is increased. It appears then that in their passage through the containing gas, the positively charged active deposit particles may become neutralized, and in fact may even become reversed in sign. To account for the increase in the ratio observed at the low pressure, it must be remembered that at the moment of formation the active deposit particles have a very high velocity. Rutherford\* has suggested that a certain number of collisions may therefore be necessary to reduce their speed so that the electric field may be capable of directing them to the electrodes; hence as the distance of the plates from the actinium is increased at the low pressure, their total activity should increase, as is found to be the case.

It might be expected that if the distance of the plates from the actinium were made sufficiently large, even at the lower pressure, similar effects to those obtained at the high pressure would be observed. With the small cylinder described this was not possible; a larger one 40 cms. long and 7.5 cms. diameter was used, and experiments at an intermediate pressure (1.2 cms.) were conducted in an exactly similar way to that

already described.

The numerical data are collected in Table III. and reproduced graphically in fig. 5.

TABLE III.

Distance :		Ratio of Activitie Negative Positive
1.0 cm.		26
3.5		44
4.7		62
8.0		76
11.0	*******	82
18.0	•••••	63
25.7		37
30.5		25

<sup>\* &#</sup>x27;Radioactivity,' p. 319.

The amount of active deposit obtained on the plates decreased as their distance from the actinium was increased, but the rate

of decrease was different for the two plates.

Inspection of the figure shows that at first there is an increase in the ratio of negative to positive activity as at the lower pressure, which subsequently shows a decrease similar to that observed at the high pressure.

Fig. 5.—1.2 cms. pressure.

80 70-60 30 30 40 40

5 10 15 20 25 30 DISTANCE IN CMS.

It must be noted that in the region between 11 and 18 cms. from the actinium it was impossible to obtain concordant results, sometimes a high and sometimes a low value for the ratio resulting.

It has been observed by Debierne in the paper already referred to, that there is a position of maximum activity in a vessel containing a preparation of actinium, but the writer does not know whether the experiments here described have

any bearing on that point.

10

The question arises as to whether the apparent loss of the positive charge of the particles can be explained by their diffusion to the sides of the vessel, but considering the relatively small distance travelled necessary for the observed effects, it is difficult to see how loss by diffusion can account for them; moreover, it would not explain the marked increase in the activity of the positive plate in the experiments at atmospheric pressure.

#### Conclusion.

It may be useful here to draw attention to some of the differences that have been observed in the transmission in electric fields of the active deposits of the different radioactive substances.

In dry and dust-free air at atmospheric pressure the active deposit of Thorium is almost completely confined to the negative pole; on reduction of the gaseous pressure to a few mms. a marked diminution in the amount transmitted to the negative pole is observed, some of the active deposit then being found on the positive boundary of the system.

In the case of Radium the transmission of its active deposit to the negative pole is not so complete as with thorium; at atmospheric pressure about 95 per cent. of the active deposit is directed to the negative pole, the remaining 5 per cent. going to the positive pole. With reduction of the gaseous pressure similar effects are observed to those mentioned for thorium, the activity of the negative boundary decreasing, that of the positive increasing.

With Actinium the active deposit may at atmospheric pressure be almost completely directed to the negative pole, but by suitable variation of the experimental conditions, the distribution may be rendered much less complete, the amount obtained on the negative pole being reduced to as little as twice that on the positive.

At low pressures, there is the same possibility of the phenomena observed depending on experimental conditions.

From the results of several independent observers it seems clear that the electrical charge exhibited by the active deposit particles of the radioactive substances is mainly determined by the numerous collisions between these particles and the ions or molecules of the gas with which they are mixed.

Whether the active deposits are electrically charged at the moment of formation from the emanations, still remains an open question. Although experiments with the active deposit from Radium show that at very low pressures (about 01 mm.) almost as much is directed to a positive as to a negative pole, this does not preclude the possibility of the active deposit particles being really positively charged, for at this pressure the velocity of the particles is so high that no ordinary electric field would be capable of directing them to the negative boundary of the system.

LXVII. On Molecular Aggregations produced in Gases by Sudden Cooling. By GWILYM OWEN, M.A., M.Sc., Assistant Lecturer and Demonstrator in Physics, and A. Ll. Hughes, B.Sc., Oliver Lodge Fellow, University of Liverpool\*.

In the Phil. Mag. for Oct. 1907 we described some experiments which showed that certain gases after passing through a process of severe cooling contained large numbers of nuclei, the presence of which was shown by their ability to act as centres for the condensation of supersaturated water vapour. The following paper is an account of the continuation of those experiments.

# I. THE CONDITIONS GOVERNING THE PRODUCTION OF THE NUCLEI.

In the paper referred to, it was shown that the gas had to be cooled below a certain temperature (which we called the "critical temperature") before the nuclei were produced. Since the term "critical temperature" has another meaning in Physics, it may be advisable to avoid using this term in future; we shall therefore throughout this paper employ the term "nucleating temperature" instead.

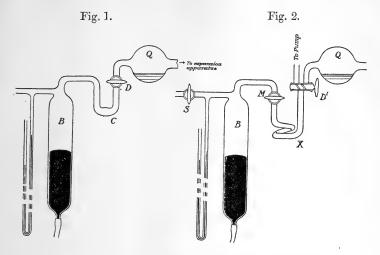
As stated in the previous paper, the number of nuclei produced depends upon the pressure of the gas and the temperature to which it is cooled. We have since found that the effect depends also upon the rate at which the gas is cooled. In fact the predominating factor in the formation of the

nuclei appears to be suddenness of cooling.

It may be well here to describe the modification of the original apparatus which enabled the cooling of the gas to take place very rapidly. Figure 1 represents the original type of apparatus used. In performing an experiment, the bend C (which we call the "tester") was surrounded by a cold liquid and as the temperature of the gas fell, the pressure was kept constant at any desired value by running the mercury up in the reservoir B. Fig. 2 represents the new form of apparatus designed to allow the gas to be very suddenly cooled. As is seen from the diagram the tester X is made in the form of a spiral. A glass tap M is introduced between the tester and the reservoir B, while the tap D is replaced by a three-way tap D'. This new form of apparatus was used as follows:—With M closed, the tester is first

<sup>\*</sup> Communicated by the Authors.

exhausted through D' to a low pressure by means of a waterpump and is then surrounded by the cold liquid. When the



tester has attained the temperature of the liquid, the tap M is quickly turned and the gas rushes from B into it while the mercury is run up to bring the pressure to the desired value. After some thirty seconds, during which the temperature has risen about one degree, the cooling liquid is removed. The gas is then given a minute and a half to regain its normal temperature; at the end of which it is driven into the cloud-chamber Q where it is tested for the presence of This method of cooling we shall denote as the "sudden" method, while the original method may be called relatively the "slow" method. The "sudden" method of cooling possesses one great advantage over the "slow" method, viz., that it enables the temperature to which the gas is cooled to be determined much more accurately; for when the tester is surrounded by the cold liquid which is kept vigorously stirred by a small rotating screw, the temperature of the liquid rapidly rises six or seven degrees, and then remains nearly constant, rising only a degree or so per minute. With the "slow" method of cooling the mean of the initial and final temperatures (which differed by several degrees) has to be taken as the temperature to which the gas is cooled, an assumption which is perhaps hardly justifiable. But with the "sudden" method the gas is not admitted into the cooled evacuated tester until the temperature of the latter has become practically constant. Thus, by this new method, any given experiment can be repeated time after time with the certainty of always dealing with the same temperature to within half a degree. Consequently the results obtained by this method are much more consistent

than those obtained by the original "slow" method.

The temperature of the cooled petroleum ether was given by a pentane thermometer reading down to the temperature of liquid air. The thermometer is correct at  $0^{\circ}$  and  $-190^{\circ}$  but is incorrect at intermediate temperatures, having a maximum error of  $12^{\circ}$  at  $-100^{\circ}$ . The temperatures therefore given in the previous paper, especially those for  $CO_2$ , require correction. In the present paper corrected temperatures are given.

# Comparison of the Effects obtained in Air by the "Sudden" and "Slow" Methods of Cooling.

The air was drawn from outside through potassium permanganate, soda lime, P<sub>2</sub>O<sub>5</sub> and a spiral six feet long immersed in liquid air and then through a plug of cotton wool.

The following table shows the effects obtained at different temperatures by the two methods:—

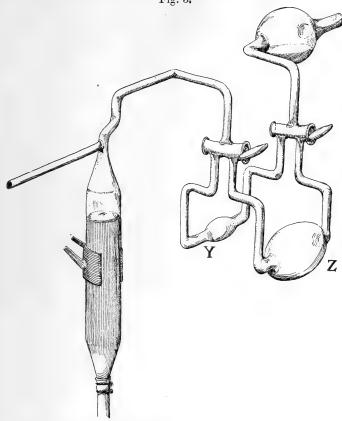
Table I.
(Tester X. Vol. 3 c.c.)

Temperature.	"Sudden" Method.	"Slow" Method.
-126° C	0	0
−131° C	Few drops.	0
-135°	Fair shower.	0
-140°	Good shower.	0
-145°	Heavy shower.	Fair shower.
-190°	Tinted rain-cloud.	Rain cloud.

The above table illustrates two facts:—The more sudden the cooling the higher is the "nucleating temperature" and the larger is the number of nuclei produced at any given temperature.

In the course of the experiments it was noticed that the values of the "nucleating temperatures" obtained depended somewhat upon the shape and size of the tester used. In order to investigate this effect systematically, the double

tester shown in fig. 3 was made. Y had a volume of 6 c.c. and Z of 36 c.c. The following table gives the results Fig. 3.



obtained with the apparatus in the case of air purified as described above.

TABLE II.

Temperature.	TESTER Y. 6 c.c.	TESTER Z. 36 c.c.
−75° C	0.	0.
-80°	0.	Several drops.
-86°	0.	Fair shower.
-92°	0.	Heavy shower.
-97°	Several drops.	Very heavy shower
-102°	Good shower.	
-107°	Heavy shower.	

Comparing this table with Table I. it will be noticed that the "nucleating temperature" for the spiral tester X of 3 c.c. and for the testers Y and Z are respectively -131°. -97°, - 80°. It will be noticed that there is a considerable difference between the nucleating temperatures obtained with testers X and Y while there is a much smaller difference between the values obtained for testers Y and Z, although in the latter case the ratio of volumes is 6:1 whereas in the former only 2:1. Now the internal diameter of the tube forming tester Y was 7 mm. while that of the tube forming the spiral tester X was only 3 mm. The rush of the gas into X is therefore not nearly so sudden as into the wider tube Y. On the other hand since Y and Z are both wide the difference in the rate at which the gas rushes into them will not be so marked. The above variations are therefore due, we think, not so much to the differences in the volumes of gas cooled as to variations in suddenness of cooling due to differences in the size and shape of the testers.

The different effects obtained by the "slow" and "sudden" methods of cooling, as illustrated by Table I., naturally suggested trying a very slow rate of cooling. We used the following method to cool the gas very slowly right down to

the temperature of liquid air.

The tester X with tap M open (see fig. 2) was enclosed in a stout brass box, but not actually in contact with it. Through the lid of the box passed a thermometer, and a propeller for stirring up the air inside. By surrounding the box with liquid air the temperature fell very slowly until it became almost stationary at  $-152^{\circ}$ . The box was then quickly removed and replaced by a vessel of liquid air. The whole process took about twenty minutes. The result obtained was a few drops, practically a no effect, whereas by the ordinary "slow" method a rain cloud was obtained (see Table I.). In all probability the few drops actually obtained were due to the more rapid fall of temperature from  $-152^{\circ}$  to  $-190^{\circ}$ .

### II. THE EFFECT IN PURE GASES.

## Carbon Dioxide.

In the first paper we mentioned that the effect is much more marked in carbon dioxide when some of the gas is actually solidified during the cooling process, and suggested that the nuclei are produced, not while the gas is approaching the solid state, but while subliming from the solid back again into the gaseous condition. In order to settle this point, further experiments have since been carried out

on  $CO_2$ .

The gas was prepared in two ways. In the first method it was obtained by heating pure sodium bicarbonate. It was then passed through calcium chloride, P2O5, a tight plug of cotton-wool, and finally solidified in a glass tube surrounded by a tall Dewar vessel containing liquid air. quantity of CO<sub>2</sub> was required the liquid-air vessel was lowered, and after the desired amount had sublimed the flow of gas was checked by replacing the Dewar vessel. The tube containing the solid CO, formed therefore a very convenient gas-holder of large capacity. On its way from this gasholder to the apparatus the gas passed through a plug of cotton-wool.

In the second method, the gas was obtained direct from the steel tubes in which it is supplied commercially and purified and condensed as before. The CO<sub>2</sub> obtained by

these two methods gave the same results.

It was found that the gas could be cooled to any temperature not lower than its condensing point, both by the "sudden" and "slow" methods, without a single nucleus being produced. (By the "sudden" method the gas could be cooled with certainty to within a degree of its condensing point.) As the expansions used for the detection of the nuclei (where not otherwise stated) were about 1.10 some expansions nearly large enough to catch the ions in CO<sub>2</sub> were tried, but with the same result. This proves that for CO<sub>2</sub> (in contradistinction to air) no nuclei at all are produced when the gas is suddenly cooled right down to its

condensing point.

It was found, however, that when condensation actually took place and the condensed gas was allowed to sublime, nuclei were present and their number increased with the amount of CO<sub>2</sub> which had been condensed. The nuclei obtained when CO<sub>2</sub> sublimes are considerably bigger than those obtained by cooling air or oxygen. The slightest supersaturation in the expansion apparatus caused by the adjusting of the pressuredrop preparatory to the expansion, brings down large numbers, but if care be taken to obviate the slightest fall in pressure, no drops are seen until an expansion is actually made. This means that the nuclei produced on the sublimation of the solid gas are bigger than those produced in air, but the fact that a certain degree of supersaturation (though small) is needed to initiate condensation on them proves them to be entirely different in character from that class of "chemical

nuclei" (such as those produced by intense ultra-violet light) in which clouds are formed without any supersaturation at all.

Ethylene.

Ethylene was prepared by the action of pure alcohol upon syrupy phosphoric acid and was passed through a condenser in ice, a strong solution of caustic potash, concentrated sulphuric acid, and  $P_2O_5$ . It was then condensed in the tube as described in the section on  $CO_2$ . After this liquefied gas had been allowed to boil under reduced pressure for a short time to remove any air or carbon monoxide, a quantity was distilled over into a second evacuated tube surrounded by liquid air until two-thirds of the liquid ethylene in the first tube had evaporated, the remaining third being rejected. Thus the second tube (our gas-holder for these experiments) contained ethylene of a high degree of purity.

The following summarizes the effects obtained:—

(1) The gas which comes off liquid ethylene is quite

nuclei-free.

(2) No nuclei are produced in ethylene when cooled either by the "sudden" or the "slow" methods. The temperatures tried were  $-95^{\circ}$ ,  $-110^{\circ}$ ,  $-145^{\circ}$ , and  $-190^{\circ}$ , condensation taking place at the last three temperatures.

Thus there is no "nucleating temperature" for ethylene.

### Methane.

Methane was prepared by heating sodium acetate with soda lime. The gas was passed through caustic potash, strong sulphuric acid, condensed and distilled as in the case of ethylene.

The following results were obtained:—

The gas which comes off liquid methane is nuclei-free.
 Table III. gives the results obtained in methane by the "sudden" method of cooling.

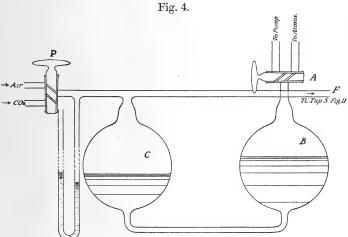
TABLE III.

Temperature.	Effect. Tester Y;
- 97° C - 102° - 107° - 112° - 131°	0. Few drops. Thin shower. Good shower. Tinted cloud.

Comparing the above with Table II. it will be seen that the effects obtained in methane are very similar to those obtained in air.

## III. THE EFFECT IN MIXTURES.

In the hope of getting further light on the origin of the nuclei we performed a series of experiments on mixtures of gases of varying proportions. Three mixtures were tried, viz., air and carbon dioxide, air and ethylene, and air and water-vapour. The apparatus shown in fig. 4 was devised to mix the gases in known proportions.



The apparatus consists of two large glass globes of  $1\frac{1}{2}$  litres capacity connected together by a glass tube. The tube F leads to tap S in fig. 2. Enough concentrated sulphuric acid is introduced to fill one globe. By means of a three-way tap A the globe B can be connected to a water-pump or to the atmosphere as desired. The mixing of the gases is effected thus:—The globe B is connected to the pump and the sulphuric acid is drawn into it to within a centimetre of the tap, which is then closed. Globe C is now exhausted through the tap D' (see fig. 2) to a pressure of about 4 cm. and air let in through P until the pressure falls a definite amount. Carbon dioxide is then admitted and, finally, more air until the pressure is atmospheric. The proportions of the constituents are determined from their respective partial pressures. Some thirty minutes are taken over this process to allow the gases to mix thoroughly. In order to diminish any inaccuracy in the estimation of the composition of the mixture due to the 4 cms. of gas originally in the globe, it is once more exhausted and the gases mixed as before. The results obtained show that this precaution was unnecessary as the effects change but slowly with the composition of the mixture. The latter could be drawn into the apparatus (see fig. 2) at approximately atmospheric pressure by connecting the globe B to the atmosphere through the tap A. About twenty tests could be performed with the mixture before the supply in the globe C became exhausted. By means of a side path (not shown) pure air could be drawn into the apparatus for purposes of comparison.

#### Air and Carbon Dioxide.

The following table summarizes the results obtained in mixtures of air and carbon dioxide.

Table IV. "Sudden" Method of Cooling.

Temperature.	Pure Air.	5 per cent. CO <sub>2</sub> .	50 per cent. CO <sub>2</sub> .
- 86° C - 92 - 96 - 127 - 128	0 0 0 Few drops. Thin shower. Tinted cloud.	0 0 Few drops. Thin shower. Tinted cloud.	0 Fair shower. Good shower.

It will be seen from the above table that the effects in pure air and air mixed with 5 per cent. of CO<sub>2</sub> are indistinguishable both in respect to the value of the "nucleating temperature" and to the magnitude of the effects obtained.

In the above experiments the mixture was maintained at a pressure of 80 cms. Thus the partial pressure of the  $\mathrm{CO}_2$  in the 50 per cent. mixture at atmospheric temperature was 40 cms. At this pressure the condensing temperature is approximately  $-85^{\circ}$ ; on cooling down, however, the partial pressure of the  $\mathrm{CO}_2$  when near the condensing point would be less than 40 cms., and therefore its condensing temperature would be somewhat below  $-85^{\circ}$ . Now from the above table it is seen that the effect in the 50 per cent. mixture starts somewhere between  $-86^{\circ}$  and  $-92^{\circ}$ . On making allowance for the reduced partial pressure, it is seen that  $\mathrm{CO}_2$  in the

mixture behaves just the same as if the air were absent, the nuclei being produced only when condensation occurs.

The same result is borne out by experiments performed

with a mixture containing 90 per cent. of CO<sub>2</sub>.

That the effects in pure air and air mixed with 5 per cent. of  $CO_2$  are practically indistinguishable is sufficiently accounted for by the fact that only very few nuclei would in any case be produced by the complete condensation and subsequent sublimation of the small quantity of  $CO_2$  present in this mixture.

#### Air and Ethylene.

As pure ethylene itself gives no effect at all when cooled to every temperature we have tried, the effect in air mixed with ethylene was investigated.

The following table shows the results obtained in three

different mixtures of air and ethylene.

TABLE V.

Temp.		Air.	5 per cent. Ethylene.	50 per cent. Ethylene.	90 per cent. Ethylene.
-125° C		0	0	t	
-127		0	Few drops.		
-128		Very thin shower.	Thin shower.	0	0
-131	•••	Thin shower.	Good shower.		0
-133	•••	Good shower.	Good shower.	Fair shower.	Very thin shower.
-143		Heavy shower.	*********		Heavy shower.
-190	•••	Tinted rain-cloud.	*********	Tinted rain-cloud.	Tinted rain-cloud.

Here again it will be noticed that the effects in pure air and in air mixed with 5 per cent. of ethylene are practically identical. The "nucleating temperature" in the mixture, it is true, is a few degrees higher than for pure air, but the difference is not sufficiently marked for any great importance to be attached to it. On the other hand, the results in a 50 per cent. mixture are readily understood, the effects obtained being simply those which would be obtained in air at a pressure equal to its partial pressure in the mixture.

The nucleating temperature in the 90 per cent. mixture bears out the same view. It will be seen, however, from the table that when the 90 per cent. mixture is cooled by liquid air just as many nuclei were produced as in the case of pure

air. Now considering the fact that ethylene itself is ineffective in the production of nuclei and the total quantity of air in this mixture is small, this is somewhat surprising. This may possibly be accounted for by the fact, that when the tap between the reservoir and the evacuated tester in liquid air is opened, the instantaneous condensation of the ethylene that takes place carries the air so rapidly into the tester that the latter is subjected to an extremely sudden fall of temperature.

# Water-Vapour in Air and CO2.

In the experiments described in the previous paper we had taken great care to obtain the gases quite dry. Since then

we have examined the effect in wet gases.

An apparatus was devised in which the gas after having been thoroughly dried could be drawn through either of two paths before entering the reservoir and tester. In one path was an arrangement by which the gas bubbled through water, thus saturating it with water-vapour. With dry air the effects started at about  $-129^{\circ}$ . With wet air we obtained a very small effect (never more than a "few drops") at temperatures between  $-122^{\circ}$  and  $-129^{\circ}$ . At temperatures below the "nucleating temperatures" the effects in dry and wet air were identical.

With wet CO<sub>2</sub> we obtained a small effect (a "very thin shower") at some five or seven degrees above the condensing-point, whereas with dry CO<sub>2</sub> no effects were obtained unless condensation occurred, as has been described above. But below the condensing temperature the effects in wet and dry

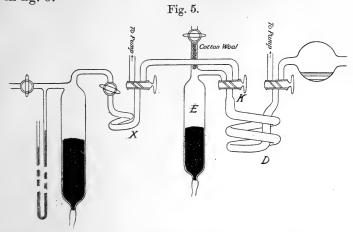
CO<sub>2</sub> were indistinguishable.

# IV. THE PERSISTENCY OF THE NUCLEI AT DIFFERENT TEMPERATURES.

#### Air Nuclei.

It had often been noticed that when air containing nuclei produced by sudden cooling was left over night in the tester, no effect was obtained on passing it into the cloud-chamber on the following morning, showing that the nuclei had in some way or other disappeared. On making a similar experiment with dusty air from the room there was only a small diminution in the effect in the same interval of time. This led to a more thorough investigation of the persistency of the nuclei. Several forms of apparatus were tried, but the

form found to be most suitable for these experiments is shown in fig. 5.



The tester used was the spiral tester of volume 3 c. c. The nuclei were produced in this by the "sudden" method of cooling, the temperature being that of liquid air. They were then driven into the evacuated spiral "oven" D of capacity 35 c.c., where they were kept for different lengths of time and at different temperatures. From this "oven" they were finally driven into the cloud-chamber by means of filtered air from the auxiliary reservoir E.

The following table illustrates the rate at which the air nuclei disappear at atmospheric temperature and pressure.

TABLE VI.

Effect obtained.
Tinted rain-cloud,
Heavy shower.
Thin shower.
Several drops.
0

We next compared the persistency of the nuclei at different temperatures. The "oven" could be maintained at any desired temperature up to 200° C. by hot glycerine. In order to have initially in the "oven" always the same number of nuclei the nucleated gas was driven into it at

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atmospheric temperature, and immediately the tap K was closed, the "oven" was surrounded by hot glycerine for a definite length of time. A similar experiment was then made in which the "oven" was kept at atmospheric temperature for the same time. Before admitting into the cloud-chamber, the gas in the "oven" was allowed one minute in which to regain atmospheric temperature.

Table VII. compares the persistency of air nuclei at

different temperatures.

TABLE VII.

Time and Temperature in "Oven."	Effect.	Time and Temperature in "Oven."	Effect.
2 min. at 15°	Heavy shower.	1 min. at 100°. 1 min. at 15°.	Fair shower.
4 min. at 15°	Good shower.	3 min. at 100°. } 1 min. at 15°. }	Very thin shower.
9 min. at 15°	Few drops.	8 min. at 100°. 1 min. at 15°.	0

Time and Temperature in "Oven."	Effect.
1 min. at 185°· 1 min. at 15°. }	Fair shower.
2 min. at 185°. 2 min. at 15°.	. 0

The above table shows clearly that keeping the nuclei at a high temperature aids their disappearance. This suggested that the nuclei would be still more persistent if kept at a low temperature. This was verified, for it was found that after thirty minutes at  $-75^{\circ}$  a fair shower was obtained which is greater than the effect obtained after a much shorter period

at 15° (see Table VI.).

Thus raised the interesting question as to whether the nuclei would persist indefinitely if kept at a temperature at which they were produced. To investigate this point an experiment was carried out with tester Z (see fig. 3). When the nuclei were produced by the "sudden" method at the temperature of liquid air, the effect obtained a minute and a half later was a thick white fog. On producing the nuclei in the same way, but keeping them for two hours in the tester

surrounded by liquid air, the effect now obtained was only a "fair shower"; this shows that, provided a sufficiently long time be given, the nuclei disappear even at the temperature of production.

#### Carbon Dioxide Nuclei.

Table VIII. shows the rate of disappearance of CO<sub>2</sub> nuclei at 15° and 80 cms. pressure, the nuclei having been produced by the sublimation of CO<sub>2</sub> solidified by liquid air.

#### TABLE VIII.

Time in "Oven" at 15°.	Effect.
20 secs	Tinted rain-cloud. Rain cloud. Very heavy shower. Good shower.

The following Table IX. shows the effect of high temperature upon the life of these nuclei. In this case, the nucleated CO<sub>2</sub> was driven into the "oven" at a pressure of 55 cms. The showers are therefore not so dense as those given in Table VIII.

#### TABLE IX.

Time and Temperature in "Oven."	Effect.	Time and Temperature in "Oven." Effect.
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Heavy shower.	$2\frac{1}{2}$ min. at $15^{\circ}$ Dense shower.
$\left[\begin{array}{cccccccccccccccccccccccccccccccccccc$	Fair shower.	$4\frac{1}{2}$ ,, $15^{\circ}$ Heavy shower.
$\begin{bmatrix} 10 & ,, & 185^{\circ} \\ 1\frac{1}{2} & ,, & 15^{\circ} \end{bmatrix}  \dots$	Very thin shower.	11½ ,, 15° Good shower.

Evidently the disappearance of the CO<sub>2</sub> nuclei is also aided by high temperature. Comparing Table VIII. with Table VI. we see that the CO<sub>2</sub> nuclei are somewhat more persistent than air nuclei.

## V. ELECTRICAL CONDITION OF THE NUCLEI.

Experiments were made to see if the nuclei were electrically charged. Nucleated air produced by cooling to the temperature of liquid air was passed into a chamber in which it could

be subjected to an intense electric field. This chamber was a glass tube about 10 cms. long and 3 cms. in diameter. Inside was a closely fitting brass tube of nearly the same length, which in turn surrounded a thick brass rod coaxial with it. There was thus left an annular space about 5 mm. wide between the brass tube and the central rod. Most of the gas driven into the tube was located in this space. After remaining in this space for one minute under the action of different electric fields, the nucleated air was driven into the cloud-chamber. The effect was found to be the same whether the electrodes were both earthed or at potential-differences of 230, 1000, or 4000 volts.

This proves the nuclei to be uncharged.

#### VI. DISCUSSION OF RESULTS.

The additional investigations published in this paper have not furnished evidence necessitating a change in the views expressed in the previous paper. Still much remains obscure and difficult to account for completely. We restate our

explanation of the effects as follows:—

When the temperature of the gas falls sufficiently, and not too slowly, molecular aggregations are formed, most probably of those slowly moving molecules whose kinetic energy is less than their mutual potential energy. On the kinetic theory, this means of course that the aggregations approximate more to the liquid phase than to the gaseous. Possibly the effects may be regarded as pointing to incipient liquefaction taking place in the gas at a temperature well above the real liquefying temperature.

The number of molecular aggregations is increased to a remarkable degree by increasing the suddenness of cooling. We find this difficult to explain, possibly it may be connected with the *irreversibility* of the phenomenon as evidenced by

their persistency.

It has already been stated that the nuclei are of considerable size. This does not necessarily mean that smaller nuclei are not produced under the same circumstances, for such aggregations might be produced but, owing to smaller stability, have disappeared before the expansion can be made.

The more rapid disappearance of the nuclei at higher temperatures is readily explained by the more vigorous bombardment of the aggregations by the molecules of the

heated gas.

The results in CO<sub>2</sub> are interesting as they suggest a fundamental difference between evaporation from the liquid

phase and sublimation from the solid. We have found that the gas evolved from liquid air, oxygen, ethylene, methane is nuclei-free, confirming the ordinary view that the evaporation of a liquid consists in the escape of separate molecules. But the fact that a mass of solid CO<sub>2</sub> (previously condensed in a perfectly dust-free state) continues to give off gas containing enormous numbers of nuclei until the whole mass has disappeared, suggests that the sublimation of solid CO<sub>2</sub> (and possibly of other substances which can pass from the solid direct into the gaseous phase) consists in the escape of separate molecules together with numerous molecular aggregations.

We will in conclusion meet some possible objections to the above views. As the effects obtained are larger when the gas is allowed to rush into the cooled evacuated chamber it might be urged that the nuclei are simply dust particles dislodged from the walls of the vessel by the sudden rush of gas. This view, however, is quite untenable from the following considerations:—(1) The effect shows no signs at all of diminution however often the experiments are made with any particular tester. (2) No effect is obtained when the gas rushing into the evacuated tester is pure ethylene, whereas a considerable effect is obtained when the ethylene contains a small percentage of air. (3) The nuclei are rapidly destroyed at a temperature of about 200° C.

Nor can it be argued that the nuclei are due to insufficient drying of the gases, as there is very little difference between the behaviour of wet gases and of those dried with the utmost

precautions.

Then again it might be urged that the nuclei are due to the presence of some impurities in the gases. This point was discussed in the previous paper. If the impurity be, let us imagine, CO<sub>2</sub> it is not likely that the effects in purified air and in air mixed with five per cent. of CO<sub>2</sub> would be indistinguishable as was found to be the case (see Table IV.).

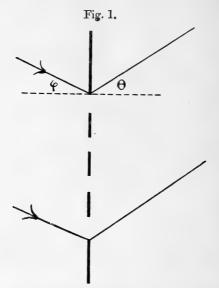
Supposing on the other hand the impurity to be some gas only slightly more easily liquefied than air, we meet with the same difficulty in accounting for the production of the nuclei in this impurity as we do in the case of air. If the effects are due to some impurity, then the only gas we obtained pure must have been ethylene. The precautions which we have taken, however, to obtain pure gases, especially in the case of oxygen and air, render this "impurity" explanation highly improbable, certainly not more probable than the view we have expressed above.

George Holt Physics Laboratory, The University of Liverpool. LXVIII. On the Effect of the Position of the Grating (or Prism) upon the Resolving Power of a Spectroscope. By Alfred W. Porter, B.Sc., Fellow of and Assistant-Professor of Physics in University of London, University College\*.

THIS paper is an extension of an interesting paper by Mr. H. Morris-Airey in this Journal for March 1906 (p. 414). In that paper it was shown that even wide slits may be employed if the light fall at nearly grazing incidence upon a grating or prism. But the closeness together of two spectral lines of different wave-length also varies with the position of the grating; and it is necessary to examine the variation of this proximity before it can be definitely decided that a gain in purity is obtained by inclining the grating or prism.

We will consider in detail the case of a grating:—

Let  $\phi$  be the angle of incidence of the light from the collimator upon the grating and  $\theta$  the angle of diffraction; both measured positive when on the same side of the normal.



Then, if e is the grating-interval, and n the order of spectrum referred to,

$$e\left(\sin\theta+\sin\phi\right)=n\lambda.$$

The effect of the finiteness of the width of the slit is allowed for by considering a small variation in the angle of incidence

\* Communicated by the Author.

 $\phi$ . The angular width of the image resulting therefrom is given by  $\Delta\theta$  where

 $-\frac{\Delta\theta}{\Delta\phi} = \frac{\cos\phi}{\cos\theta}.$ 

It must be observed that whether this decreases or not as  $\phi$  decreases can only be decided when it is known which side of the normal the image is on.

Two spectral lines for which the wave-lengths differ by

 $\delta\lambda$  will be at an angular distance apart  $\delta\theta$  where

$$\frac{\delta\theta}{\delta\lambda} = \frac{n}{e\cos\theta}.$$

In these formulæ,  $\Delta\theta$  is a measure of the broadness of each image and  $\delta\theta$  is the separation between the centres of neigh-

bouring images (or dispersion).

Now, in estimating the purity of the spectrum, it is clearly the ratio of the second to the first of these two quantities which is important. Greater broadening of the image would be consistent with greater purity if the dispersion was increased in proportionately greater amount. The ratio of

$$\frac{\delta\theta}{\delta\lambda}$$
 to  $-\frac{\Delta\theta}{\Delta\phi}$ ,

a ratio which may be spoken of as the tilt-advantage, is

$$A = \frac{n}{e \cos \phi};$$

whence it is seen that the advantage of the arrangement increases as  $\phi$  increases, whether the spectrum examined is on the same side of the normal as the incident beam or not. The relative advantage compared with the case of normal incidence is  $1/\cos \phi$ .

In illustration of the meaning of this result, it may be pointed out that the case in which greatest separation between the centres of the images is obtained is not the case in which greatest advantage is gained. Greatest separation between the centres occurs when  $\cos \theta = 0$ ; that is when

$$e(1 + \sin \phi) = n\lambda$$
.

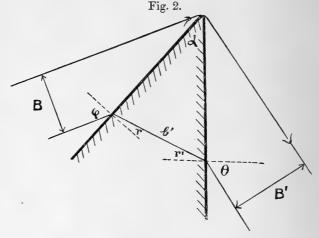
This case can be obtained by starting from normal incidence, selecting any spectrum and turning the grating so as to increase  $\theta$  numerically. The relative advantage in this case can be only moderate. On the contrary, in order to increase the angle of incidence to 90°, the grating must be turned the other way; in this case greater purity is obtained although

the dispersion is not nearly so great. This latter is the case in which very wide slits may advantageously be used.

The corresponding equations in the case of a prism are:

$$-\frac{\Delta\theta}{\Delta\phi} = \frac{\cos r' \cos \phi}{\cos r \cos \theta} = \frac{B}{B'}$$
$$\frac{\delta\theta}{\delta\mu} = \frac{\sin \alpha}{\cos \theta \cos r} = \frac{b'}{B'}$$
$$A = \frac{\sin \alpha}{\cos r' \cos \phi} \frac{d\mu}{d\lambda} = \frac{b'}{B} \frac{d\mu}{d\lambda}$$

where  $\mu$  is the refractive index and the other data are explained by the accompanying figure.



Occasionally the question of purity may not be the most important one. It is notorious that the focal length of the telescopes usually furnished with spectroscopes is almost always much less than it advantageously might be. In a particular single-prism spectroscope which I have in mind, the sodium lines  $(D_1D_2)$  are only just separable when the prism is in the position of minimum deviation. This is simply not owing to a lack of purity, but because the ultimate images are so close together that it would be impossible to detect intermediate images (with the telescope provided), if such existed, because the separation is below the minimum visible. By turning the prism so as to increase the angle of emergence, the dispersion becomes so great that in spite of the simultaneous increase in he breadth of each line one would easily detect several intermediate lines.

LXIX. Note on certain Dynamical Analogues of Temperature Equilibrium. By G. H. Bryan (Bangor)\*.

In the Archives Néerlandaises for 1900 (Livre jubilaire dédié à M. H. A. Lorentz) I described under the title of "Energy Accelerations" a method of studying problems dealing with the partition of energy in systems of particles in which some kind of statistical equilibrium exists. This method consists essentially in writing down expressions for the second differential coefficients with respect to the time of the squares and products of velocities or momenta of the system considered.

The method in question appears to have been previously employed by Mr. Burbury, who, however, did not employ the term "energy-accelerations" in connexion with the second

differential coefficients in question.

I was, and still am, of opinion that a further study of energy-accelerations must have an important bearing on all problems in the Kinetic Theory dealing with questions of temperature-equilibrium, and the fact that no attempt seems to have been made to follow the problem up, may be taken as evidence of the large congestion of unsolved problems which presses heavily on the shoulders of the mathematician of to-day. The present note deals with two simple applications which happened to remain unnoticed when the paper was written.

Consider in the first place an ideal medium formed of material particles uniformly distributed in space, both as regards position and as regards direction, and attracting or repelling one another according to any law of force as a function of the distance between them.

If we confine our attention to one particular particle, the effect of the other particles will be to produce varying fields of force acting on the particle in question. Take now the equation of energy-accelerations which may be written in the more general form:—

$$\frac{d^2}{dt^2}(\frac{1}{2}mu^2) = \frac{1}{m}\left(\frac{d\mathbf{V}}{dx}\right)^2 - u\frac{d^2\mathbf{V}}{dt\,dx} - u^2\frac{d^2\mathbf{V}}{dx^2} - uv\frac{d^2\mathbf{V}}{dx\,dy} - uw\frac{d^2\mathbf{V}}{dx\,dy},$$

where u, v, w stand for velocity components, V the potential

of the field due to the other particles.

The assumption that the field produced by the other particles is independent of the motion of the particle under consideration, and that this field has on an average no directional properties, shows that the mean values of the last two terms vanish, and the assumption that a stationary state

<sup>\*</sup> Communicated by the Physical Society: read March 13, 1908.

exists requires that the mean value of the term  $ud^2V/dt\,dx$  should also vanish, reducing the energy-acceleration equation in this case to the ordinary standard form, brackets denoting mean values:—

$$\left[\frac{d^2}{dt^2}(\frac{1}{2}mu^2)\right] = \frac{1}{m}\left[\left(\frac{d\mathbf{V}}{dx}\right)^2\right] - \left[u^2\right]\left[\frac{d^2\mathbf{V}}{dx^2}\right].$$

For energy equilibrium the left-hand side must vanish. This is only possible when the mean value of  $d^2V/dx^2$  is positive. Now the assumed absence of directional properties, or in other words the assumed isotropic character of the medium, requires that the average values of  $d^2V/dx^2$ ,  $d^2V/dy^2$ , and  $d^2V/dz^2$  shall be equal; therefore each is equal to one-third the average value of  $\Delta V$ . We conclude that statistical energy equilibrium cannot exist in a system of particles possessing the assumed properties unless  $\Delta V$  is positive.

For the Newtonian law of force  $\Delta V = 0$ . In this case the mean value  $\left[ \frac{d^2V}{dx^2} \right]$  therefore also vanishes, and the

energy-acceleration equation takes the form:-

$$\left[\frac{d^2}{dt^2} \left(\frac{1}{2}mu^2\right)\right] = \frac{1}{m} \left[\left(\frac{d\mathbf{V}}{dx}\right)^2\right].$$

This shows that the only kind of statistical equilibrium is the statical state of unstable equilibrium defined by dV/dx=0, dV/dy=0, and dV/dz=0 on each particle, and in the absence of this state an acceleration of kinetic energy will take place.

It is thus impossible with the Newtonian law to build up a medium of material particles, either attracting or repelling one another, and possessing properties of energy equilibrium

analogous to those of a system of gas molecules.

It need not be pointed out that this investigation does not preclude the possibility under the Newtonian Law, of stationary motions such as those occurring in the solar

system.

Exactly the same conclusions hold good if the law of force is such as to make  $\Delta V$  negative. The equations of energy equilibrium here require the further condition that  $\begin{bmatrix} u^2 \end{bmatrix} \begin{bmatrix} v^2 \end{bmatrix} \begin{bmatrix} w^2 \end{bmatrix}$  should be zero, which can only happen if the system always remains at rest.

The necessary condition  $\Delta V > 0$  becomes, for the particular case in which the field is due to an attracting particle placed

at the origin,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dV}{dr}\right) > 0,$$

showing that  $r^2dV/dr$  must increase with r. In other words, the force if repulsive must vary according to a higher power

of the inverse distance than the square (the inverse fifth power would represent a possible law of force if repulsive). If the force is attractive it must vary according to a lower

power of the inverse distance than the square.

The second point to be noticed is that unless the expression for the kinetic energy of a dynamical system is a quadratic function of the velocities with constant coefficients, the equations of energy equilibrium no longer assume the form of linear relations connecting the mean squares and products of velocities, but they also involve terms of the fourth degree in these velocities. An illustration of this fact is afforded by the motion of a particle in a plane when referred to polar coordinates. If we write down the expressions for the energy-accelerations

$$\frac{d^2}{dt^2}(\frac{1}{2}\dot{r}^2)$$
 and  $\frac{d^2}{dt^2}(\frac{1}{2}r^2\dot{\theta}^2)$ 

in terms of the velocities and coordinates, using the equations of motion

$$\ddot{r} - r\dot{\theta}^2 = -\frac{dV}{dr}$$
 and  $\frac{1}{r}\frac{d}{dt}(r^2\dot{\theta}) = -\frac{dV}{rd\theta}$ 

we shall obtain expressions involving the velocity components up to the fourth degree, and the energy components therefore up to the second degree. The conditions of energy equilibrium between the transversal and radial components will therefore no longer take the form of linear relations connecting the mean values of the energy components in question.

On the other hand, when we refer the motion to x and y coordinates, the equations of energy equilibrium are linear in

the energy components.

It appears, therefore, that if dynamical systems are to represent the phenomena of temperature-equilibrium consistently with the commonly accepted hypothesis that temperature is a quantity of the nature and dimensions of molecular kinetic energy, the expression for the kinetic energy must in general have constant coefficients or must at least satisfy certain conditions which are fulfilled in the case of constant coefficients. While the analogy of kinetic energy with temperature may hold good in the case of a system of particles, there must exist dynamical systems for which this analogy does not hold good. As a purely negative conclusion this result is not inconsistent with Stefan's law in which we have the energy of radiation proportional to the fourth power of the energy of molecular motion. But whether it is possible to construct a dynamical model whose energy-partition is analogous to Stefan's Law must be a question for future investigation.

LXX. Notices respecting New Books.

Bulletin of the Bureau of Standards. Vol. IV. No. 3, Jan. 1908. Washington: Government Printing Office, 1908.

THE contents of this issue include an important paper by W. A. Noyes and H. C. P. Weber on the Atomic Weight of Chlorine. The method employed consists in weighing the hydrogen absorbed in palladium and the chlorine in the form of potassium chloroplatinate. The hydrogen is passed over the heated chloroplatinate, hydrochloric acid being formed which is condensed and weighed.

The mean value found is 35.184 (H=1).

The part contains also a critical paper by W. W. Coblentz on instruments and methods used in radiometry, in which the relative merits are discussed of a radiomicrometer, linear thermopile, radiometer and bolometer. The thermopile is recommended on account of its greater steadiness for measuring very weak sources of radiation, e. g. the extreme ultra-violet and infra-red region of the spectrum. The other articles are the preparation of chloroplatinic acid by electrolysis of platinum black, by H. C. P. Weber; the self-inductance of a coil of any length and any number of layers of wire, by E. B. Rosa; the self-inductance of a solenoid of any number of layers, by Louis Cohen; a quartz compensating polariscope with adjustable sensibility, by F. Bates.

## LXXI. Intelligence and Miscellaneous Articles. ON THE MIXING OF GASES.

To the Editors of the Philosophical Magazine.

GENTLEMEN,— REGRET that my absence in Egypt during February and March prevented my seeing Professor Orr's paper in your February number till quite recently. I have since contributed to 'Science Progress' an article in which my views on the questions which he raises are explained more at length. I do, however, doubt whether there is any proof that the mixture of two gases by diffusion is an irreversible process. It is of course true that if we have two mixtures of (say) oxygen and nitrogen at the same pressure and temperature, in one of which oxygen, and in the other nitrogen, preponderates, then if we remove the partition which separates them, they at once begin to mix more uniformly. But as that would equally be the case if the process of diffusion were periodic, the observed fact is no proof that the process is not periodic. Theoretically I maintain that no irreversible motion is possible among the molecules of a gas, if the kinetic theory be true, and if the gas be completely isolated, that is completely protected from the influence of external bodies. Professor Orr, as I gather, will not accept the kinetic theory. In that he may be right. But if we do not accept it, is there any other theory that can be applied?

To prove experimentally that the diffusion process is irreversible would require that the experiment be continued for a time at least half as long as the period of the motion if it were periodic. How long a time would Professor Orr consider sufficient? Also to make the experiment at all conclusive, the diffusing gases must at every instant during the experiment be completely protected from all external influences. Has such an experiment ever been made?

S. H. BURBURY.

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## END OF THE FIFTHTEENTH VOLUME.

