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IV. *The Diffusion of Ions into Gases.*

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*Communicated by Professor J. J. THOMSON, F.R.S.*

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## INTRODUCTION.

THERE are several interesting results in connection with molecular physics which can be obtained from the coefficients of diffusion of ions into gases. From determinations of these coefficients we are enabled to find the number of molecules in a given volume of a gas, and to compare the charge on an ion in a conducting gas with the charge on a hydrogen ion in a liquid electrolyte. In the present paper the principles which are involved in the theory of the interdiffusion of gases are applied to the diffusion of ions produced in a gas by the action of Röntgen rays.

It will simplify matters if we first consider the general theory of the conductivity of gases. Professor THOMSON has shown that all the phenomena which are met with can be explained by supposing that the rays produce ions in the gas, the motion of which, when acted on by an electric force, gives rise to the observed conductivity. When the gas has been removed from the influence of the rays the conductivity gradually diminishes, and the disappearance of the ions may be due to three causes, any of which may predominate.

1. If an electric force is acting, the ions travel through the gas along the lines of force and are discharged when they reach the boundary.
2. Recombination destroys the conductivity; the positive and negative ions as they move about in the gas come into contact and thus neutralise one another.
3. The ions diffuse and come into contact with the sides of the vessel which contains the gas. This effect we shall denote as the effect of the sides. Like the recombination, it takes place when no electric forces are acting, and it is due to the motion of agitation of the ions.

In order to illustrate in a simple way the principles which are involved in the experiments which are described in the present paper, we will suppose that a gas is contained in a metal sphere and that it has been made a conductor by the action of

Röntgen rays. Let us consider what takes place when the gas has been removed from the action of the rays, disregarding for the present the effect of recombination. The ions may be considered as constituting a separate gas, the molecules of which may be either bigger or smaller than the molecules of the gas in which they are immersed. When an ion comes into contact with the surface of the sphere, it loses its charge, so that the metal may be regarded as a body which completely absorbs the ions. The reduction in the conductivity by the diffusion of the ions to the sides is exactly analogous to the removal of moisture from a gas by bubbling it through sulphuric acid. The more rapidly the water vapour diffuses through the gas, the greater will be the number of water molecules which come into contact with the acid round the bubble. If the quantity of moisture which is removed be found experimentally, the coefficient of diffusion of water vapour into the gas can be deduced.\* It would be impracticable to use this method to find the coefficient of diffusion of ions into a gas contained in a large vessel, as the loss of conductivity due to recombination would be large compared with the loss due to the sides.

The method which was employed was to pass a uniform stream of gas through fine metal tubing, and to allow the rays to fall on the gas immediately before entering the tubing. The bore of the tubing can be so adjusted that the number of ions which come into contact with the sides will be large compared with the number which recombine.

It is convenient to use tubing of such a length that the conductivity will be reduced to about one-half its initial value.

In order to obtain the coefficient of diffusion, when the reduction in the conductivity is known, the following problem presents itself.

If a small quantity of a gas, A, is mixed with another gas, B, and the mixture passed along a tube, the sides of which completely absorb A, to find what quantity of A emerges from the tube with B.

It will be immediately seen that if the gases diffuse rapidly into each other, a large proportion of the molecules of the gas A will come into contact with the surface of the tube, and will there be absorbed. If on the other hand the rate of interdiffusion is very small, the molecules of A will travel down the tube in straight lines parallel to the axis of the tube, and practically none of them will come into contact with the surface.

The complete solution of the above problem, taking into account the variation of the velocity at points along a radius of the tube, is given in Section I. The results of the experiments and the conclusions to which they lead are contained in Section II.

\* JOHN S. TOWNSEND, 'Phil. Mag.,' June, 1898.

## SECTION I.

## MATHEMATICAL INVESTIGATION.

1. In a conducting gas we have two distinct sets of bodies to deal with : the ions, which are charged, and whose motion under an electromotive force constitutes conduction, and the uncharged molecules, the number of which is very much greater than the number of ions [the latter number multiplied by  $10^{12}$  gives about the order of the number of molecules]. The ions, which for the present we will suppose to consist of an equal number of positively and negatively charged carriers, may be considered as a distinct gas, A, and the rest of the molecules through which they move as another gas, B, the two together constituting a conducting gas. When the carriers come into contact with a metal surface, they either give up their charge to the metal or remain in contact with the surface, so that the metal behaves like a perfect absorber of the ions.

In a paper On the Dynamical Theory of Gases,\* MAXWELL has given the general equations of motion of two gases diffusing into each other.

The equations are of the form :

$$\rho_1 \frac{du_1}{dt} + \frac{dp_1}{dx} = kA\rho_1\rho_2(u_2 - u_1) + X\rho_1,$$

where  $\rho_1$  and  $\rho_2$  are the densities of the gases ;  $p_1$  and  $p_2$  their partial pressures ;  $u_1$  and  $u_2$  their mean velocities in the  $x$  direction ;  $kA$  a constant for the two gases which depends upon the temperature ; and  $X$  the force acting on unit mass.

The first and last terms in the above equation may be omitted, as they are small compared with the other two, but in dealing with a gas which is made up of small charged bodies a new term must be introduced when electric forces are acting.

Thus the term  $\rho_1 X$  arising from the force of gravity, for example, is  $981 \times m_1 n_1$  ; where  $n_1$  is the number of molecules of the first gas per cub. centim. and  $m_1$  the mass of each ( $m_1$  expressed in grammes is of the order  $10^{-23}$ ).

In order to estimate  $dp_1/dx$  roughly, we will suppose that the gases are contained in a tube of .15 centim. radius, and that  $p_1 = 0$  at the surface. In this case  $\frac{dp_1}{dx}$  will be of the order  $\frac{p'_1}{.15}$ , where  $p'_1$  is the value of  $p_1$  at the centre. Letting  $\xi_1$ ,  $\eta_1$  and  $\zeta_1$  denote the mean velocities of agitation in the directions  $x$ ,  $y$ , and  $z$ ,  $p'_1 = m_1 n'_1 \xi_1^2$ , and we obtain  $\frac{p'_1}{.15} = \frac{m_1 n'_1 \xi_1^2}{.15}$ , which is large compared with  $981 \times m_1 n'_1$ , since  $\xi_1$  is of the order  $10^4$ .

The first term  $m_1 n_1 du_1/dt$  is small compared with  $dp_1/dx$ , since the resistance to the motion is so great ; the acceleration in the cases with which we are concerned

\* J. C. MAXWELL, 'Phil. Trans.,' vol. 157, 1866.

is less than the acceleration of a body falling under gravity, and consequently is of a much smaller order than  $dp_1/dx$ .

When each of the  $n_1$  molecules of the first gas carries an atomic charge ( $6 \times 10^{-10}$  electrostatic unit), forces come into play which may be of any order compared with  $\frac{dp_1}{dx}$ . In an electric field having a potential gradient of 1 volt per centim., the force on  $n'_1$  ions would be  $\frac{1}{300} \times 6 \times 10^{-10} \times n'_1$ , which is large compared with the above value of  $\frac{dp}{dx} \left[ \frac{10^{-15} n'_1}{\cdot 15} \right]$ .

In general six equations of the form given by MAXWELL are required, but when, as in the present case, one of the gases is present in very small quantities, the system of equations reduces to three, and the process of diffusion of the ions may be considered as having no effect on the mean velocities of the gas through which they diffuse. The second gas, B, has practically no motion in passing along a tube, except along the axis, which we take as coinciding with the axis of coordinates  $z$ . The notation can therefore be simplified, and in what follows we shall let  $n$  be the number of ions per cub. centim.;  $p$ , their partial pressure;  $e$ , the charge on each ion; X, Y, and Z, the electric forces at any point;  $u$ ,  $v$ , and  $w$ , the velocities of the ions; W, the velocity of the gas, B, through the tube; ( $\alpha$ ) the radius of the tube; and K, the coefficient of diffusion of A into B.

The differential equations giving the motion are :—

$$\begin{aligned} \frac{1}{K} pu &= -\frac{dp}{dx} + nXe, \\ \frac{1}{K} pv &= -\frac{dp}{dy} + nYe, \\ \frac{1}{K} pw &= -\frac{dp}{dz} + nZe + \frac{1}{K} pW. \end{aligned}$$

When the steady state is reached,  $p$  is constant at any point in the tube with respect to the time, and the equation of continuity becomes

$$\frac{d}{dx}(pu) + \frac{d}{dy}(pv) + \frac{d}{dz}(pw) = 0.$$

$dp/dz$  can be omitted from the third equation, as it is small compared with the other terms, thus, in practice,  $\frac{1}{p} \frac{dp}{dz}$  is of the order  $\frac{1}{20}$ ,  $W = 100$ , and  $K = \cdot 03$ ; so that  $dp/dz$  is only about one ten-thousandth of  $\frac{1}{K} pW$ .

In the case with which we are dealing,  $W = \frac{2V}{\alpha^2} (\alpha^2 - r^2)$ , where  $V$  is the mean velocity defined by the condition,  $\pi \alpha^2 V t =$  total volume of the gas B, crossing any section in a time  $t$ . Confining the investigation to the case where the numbers of

positive and negative carriers are equal, the forces X, Y, and Z vanish, and the equation for  $p$  becomes :—

$$K \left( \frac{d^2 p}{dx^2} + \frac{d^2 p}{dy^2} \right) - \frac{2V}{a^2} (a^2 - r^2) \frac{dp}{dz} = 0 ;$$

which, expressed in cylindrical coordinates, becomes

$$r^2 \frac{d^2 p}{dr^2} + r \frac{dp}{dr} - \frac{2Vr^2}{a^2 K} (a^2 - r^2) \frac{dp}{dz} = 0 \quad \dots \dots \dots (1).$$

We have to find a solution of this equation which will satisfy the conditions :

$p = p_0$  a constant when  $z = 0$  for all values of  $r$ , since A is distributed evenly throughout B on entering the tube.

$p = 0$  when  $r = a$  for all values of  $z$ , since A gets absorbed by coming into contact with the tube.

Let  $p = \phi e^{-\frac{\theta^2 a^2 K}{2V} z}$ , where  $\phi$  is a function of  $r$ , and  $\theta^2$  a constant to be determined afterwards.

Substituting this value of  $p$  in Equation (1), we obtain

$$r^2 \frac{d^2 \phi}{dr^2} + r \frac{d\phi}{dr} + \theta^2 r^2 (a^2 - r^2) \phi = 0. \quad \dots \dots \dots (2).$$

One solution, M, of this equation can be found in the form of a series.

Let

$$A_m r^m + A_{m+2} r^{m+2} + A_{m+4} r^{m+4}$$

be three consecutive terms in the expansion of M in powers of  $r$ .

Substituting in (2) we find, by equating to zero the coefficient of the  $(m + 4)^{\text{th}}$  power of  $r$ , that

$$(m + 4)^2 A_{m+4} + \theta^2 a^2 A_{m+2} - \theta^2 A_m = 0.$$

If  $A_{m+4} r^{m+4}$  is the first term in M,  $(m + 4)^2$  must vanish. Hence, the first term must be a constant, which we will take as unity. Thus

$$M = 1 + B_1 r^2 + B_2 r^4 + B_3 r^6 + \&c. \quad \dots \dots \dots (3),$$

where  $B_1, B_2, B_3, \&c.$ , are found from the equations

$$\begin{aligned} 4B_1 + \theta^2 a^2 &= 0, \\ 16B_2 + \theta^2 a^2 B_1 - \theta^2 &= 0, \\ 36B_3 + \theta^2 a^2 B_2 - \theta^2 B_1 &= 0, \&c. \end{aligned}$$

2. If Equation (3) be written in the form

$$M = 1 - \beta_1 \left(\frac{r}{a}\right)^2 + \beta_2 \left(\frac{r}{a}\right)^4 - \beta_3 \left(\frac{r}{a}\right)^6 + \&c. \dots,$$

the relation connecting any three consecutive coefficients becomes

$$4n^2\beta_n = \theta^2\alpha^4(\beta_{n-1} + \beta_{n-2}),$$

from which it is easy to see that the series we have found for  $M$  is convergent.

Let  $2n$  be greater than  $\theta^2\alpha^4$ , and let  $\beta_{n-1} + \beta_{n-2} = S$ . Then

$$\beta_n < \frac{S}{2n}, \text{ and } \beta_{n+1} < \frac{S}{2n}.$$

Similarly,

$$\beta_{n+2} < \frac{S}{2n(n+2)}, \text{ and } \beta_{n+3} < \frac{S}{2n(n+2)}.$$

Proceeding in this way, we see that

$$\beta_{n+2m} < \frac{S}{2n(n+2)(n+4)\dots(n+2m)},$$

from which it follows that the series (3) is convergent.

3. The Equation (2) has a second independent solution,  $N$ , which can be found by using the solution  $\phi = M$ , the complete solution being  $\alpha M + \beta N$ . It will be seen from what follows that, when  $r = 0$ ,  $N$  becomes infinite; so that it must be neglected when the gas  $A$ , as in the present case, extends to the centre of the tube.

Substituting for  $\phi$  in Equation (2)  $N = Mu$ , we obtain

$$Mr^2 \frac{d^2u}{dr^2} + 2r^2 \frac{dM}{dr} \frac{du}{dr} + rM \frac{du}{dr} = 0,$$

or

$$\frac{1}{du/dr} \frac{d^2u}{dr^2} + \frac{2}{M} \frac{dM}{dr} + \frac{1}{r} = 0,$$

which, on integration, gives  $rM^2 du/dr = c$ . Hence

$$u = c \int \frac{dr}{rM^2}.$$

Expanding  $\frac{1}{rM^2}$  in partial fractions, and integrating, we see that  $u$  has a term  $c \log r$ , so that  $N$  becomes infinite when  $r = 0$ .

Thus  $p$  cannot contain  $N$  in its expansion, and we get

$$p = \Sigma c_\theta M_\theta e^{-\frac{\theta^2 \alpha^2 K}{2V} z} \dots \dots \dots (4).$$

The boundary condition,  $p = 0$  when  $r = a$ , requires that such values of  $\theta^2$  be chosen as will make  $M_a = 0$  when  $r = a$ .

Substituting (a) for (r) in the function M, we obtain a function of  $\theta^2 a^4$  with numerical coefficients. Let  $x_1, x_2, x_3, \&c.$ , be the values of  $\theta^2 a^4$  which satisfy the equation  $M_{r=a} = 0$ , and let  $\theta_1, \theta_2, \theta_3, \&c.$ , be the corresponding values of  $\theta$ ; and equation (4) becomes

$$p = c_1 M_1 e^{-\frac{\theta_1^2 a^2 \kappa}{2V} z} + c_2 M_2 e^{-\frac{\theta_2^2 a^2 \kappa}{2V} z} +, \&c. \quad (5).$$

4. Before proceeding to determine the coefficients  $c_1, c_2, \&c.$ , it is necessary to prove some general properties of the solution of the equation  $\nabla^2 \phi + \theta^2 f(x, y, z) \phi = 0$ ;  $f(x, y, z)$  being any function of  $x, y, z$ . Let  $\phi_n$  and  $\phi_{n'}$  be solutions corresponding to values  $\theta_n$  and  $\theta_{n'}$  of the parameter  $\theta$ .

By GREEN'S theorem, we have

$$\iiint [\phi_n \nabla^2 \phi_{n'} - \phi_{n'} \nabla^2 \phi_n] dx dy dz = \iint \left( \phi_n \frac{d\phi'}{dv} - \phi' \frac{d\phi}{dv} \right) dS.$$

Let  $\theta_n$  and  $\theta_{n'}$  be such values of  $\theta$  as will make  $\phi_n$  and  $\phi_{n'}$  vanish at the surface S of the region throughout which the above volume integral is taken. The surface integral vanishes under these conditions, and we get, on substituting for  $\nabla^2 \phi_n$  and  $\nabla^2 \phi_{n'}$  their values,

$$(\theta_n^2 - \theta_{n'}^2) \iiint \phi_n \phi_{n'} f(x, y, z) dx dy dz = 0 \quad (6a),$$

which shows that the triple integral vanishes when  $\theta_n$  and  $\theta_{n'}$  do not coincide.

Let us suppose  $\phi_{n'}$  to be got from  $\phi_n$  by changing  $\theta_n^2$  into  $\theta_n^2 + d\theta^2$ , and GREEN'S theorem gives

$$- d\theta^2 \iiint \phi_n^2 f(x, y, z) dx dy dz = d\theta^2 \iint \left[ \phi_n \frac{d^2 \phi_n}{d\theta_n^2 dv} - \frac{d\phi_n}{d\theta_n^2} \frac{d\phi_n}{dv} \right] dS,$$

so that

$$\iiint \phi_n^2 f(x, y, z) dx dy dz = \iint \frac{d\phi_n}{d\theta^2} \cdot \frac{d\phi_n}{dv} dS \quad (6b).$$

We also have

$$\iiint \nabla^2 \phi_n dx dy dz = \iint \frac{d\phi_n}{dv} dS,$$

from which we derive

$$\theta_n^2 \iiint \phi_n f(x, y, z) dx dy dz = - \iint \frac{d\phi_n}{dv} dS \quad (6c).$$

5. Let  $f(x, y, z)$  be  $(a^2 - r^2)$  and  $\phi$  a function of the cylindrical coordinate  $r$ . The equation  $\nabla^2 \phi + \theta^2 f(x, y, z) \phi = 0$  then reduces to  $\frac{1}{r} \frac{d}{dr} \left( r \frac{d\phi}{dr} \right) + \theta^2 (a^2 - r^2) \phi = 0$ , so that we can substitute M for  $\phi$  in the three equations (6a), (6b), and (6c). If the surface integrals be taken over the surface of the cylinder of radius  $a$ , we obtain



$$\int_0^a M_n M_{n'} (\alpha^2 - r^2) r dr = 0 \quad \dots \quad (7a).$$

$$\int_0^a M_n^2 (\alpha^2 - r^2) r dr = a \left[ \frac{dM_n}{d\theta_n^2} \cdot \frac{dM_n}{dr} \right]_{r=a} \quad \dots \quad (7b).$$

$$\int_0^a M_n (\alpha^2 - r^2) r dr = -\frac{a}{\theta_n^2} \left[ \frac{dM_n}{dr} \right]_{r=a} \quad \dots \quad (7c).$$

From these three equations the coefficients  $c_1$ ,  $c_2$ , &c., can be determined.

Since  $p = p_0$ , when  $z = 0$ , we have

$$p_0 \equiv c_1 M_1 + c_2 M_2 + \&c.$$

Multiply this identity by  $M_n (\alpha^2 - r^2) r dr$ , and integrating from  $r = 0$  to  $r = a$ , we obtain

$$-\frac{ap_0}{\theta_n^2} \left[ \frac{dM}{dr} \right]_{r=a} = C_n \cdot a \left[ \frac{dM}{dr} \frac{dM}{d\theta_n^2} \right]_{r=a}.$$

Hence

$$C_n = \frac{-p_0}{\theta_n^2 \left[ \frac{dM_n}{d\theta_n^2} \right]_{r=a}},$$

and

$$p = -p_0 \left[ \frac{M_1}{\theta_1^2 \left[ \frac{dM_1}{d\theta_1^2} \right]_{r=a}} \cdot e^{-\frac{\theta_1^2 \alpha^2 K z}{2V}} + \frac{M_2}{\theta_2^2 \left[ \frac{dM_2}{d\theta_2^2} \right]_{r=a}} \cdot e^{-\frac{\theta_2^2 \alpha^2 K z}{2V}} + \&c. \right] \quad \dots \quad (8).$$

On entering the tube the quantity of the gas A, per cub. centim., is proportional to  $p_0$ , so that  $p_0 \pi \alpha^2 V$  is proportional to the quantity of A entering the tube per second (which is found by the conductivity when A consists of ions). The quantity of A which crosses a section at a distance  $z$  from the origin per second is proportional to  $\int_0^a p \times \frac{2V}{\alpha^2} (\alpha^2 - r^2) 2\pi r dr$ , where  $p$  has the value given in Equation (8). The ratio R of the quantity of A which passes a section at a distance  $z$  to that which enters the tube is

$$\frac{4}{p_0 \alpha^4} \int_0^a p (\alpha^2 - r^2) r dr.$$

Substituting for  $p$  its value and using Equation 7 (c), we get

$$R = \frac{4}{\alpha^3} \left[ \frac{1}{\theta_1^4} \left\{ \frac{dM_1/dr}{dM_1/d\theta_1^2} \right\}_{r=a} \cdot e^{-\frac{\theta_1^2 \alpha^2 K z}{2V}} + \frac{1}{\theta_2^4} \left\{ \frac{dM_2/dr}{dM_2/d\theta_2^2} \right\}_{r=a} \cdot e^{-\frac{\theta_2^2 \alpha^2 K z}{2V}} + \&c. \right] \quad \dots \quad (9).$$

The values of  $\theta$  which are admissible are roots of the equation  $M_{r=a} = 0$  regarded as an equation in  $\theta$ .

[We may here point out that, if the gas, A, on entering the tube was distributed across the section according to the law  $p = \chi(v)$ , where  $\chi$  denotes any function, the

coefficients, in the expansion of  $p$  in Equation (5), would be determinable by means of the identity

$$\chi(v) \equiv C_1 M_1 + C_2 M_2 + \&c.,$$

and by using 7 (a) and 7 (b) we see that

$$C_n' = \frac{\int_0^a \chi(r) M_n (a^2 - r^2) r dr}{a (dM_n/dr \cdot dM_n/d\theta^2)^{r=a}}.$$

Hence any function  $\chi$  can be expanded in a series of the "M" functions.

It can further be seen from Equations 6 (a) and 6 (b) that  $\chi(r)$  can be expanded in a series of functions  $\phi$ , where  $\phi$  is a solution of  $\frac{1}{r} \frac{d}{dr} r \frac{d\phi}{dr} + \theta^2 f(r) \phi = 0$ ; those values of  $\theta$  being selected which make  $\phi$  vanish at the boundary of the cylinder to which  $\chi$  applies.]

6. Before determining the roots of the equation  $M_{r=a} = 0$ , it will be found useful to establish the two following propositions:—

1. All the coefficients  $\frac{1}{a^2 \theta^4} \left[ \frac{dM/dr}{dM/d\theta^2} \right]^{r=a}$  in the expansion of R in Equation (9), are positive, and their sum is  $\frac{1}{4}$ .
2. All the roots of the Equation  $M_{r=a} = 0$  are positive.

When  $z = 0$ , R must be unity, so that

$$\sum_{n=1}^{n=\infty} \frac{1}{a^2 \theta_n^4} \left[ \frac{dM_n/dr}{dM_n/d\theta_n^2} \right]^{r=a} = \frac{1}{4}.$$

Also

$$\frac{1}{a^2 \theta_1^4} \left[ \frac{dM_1/dr}{dM_1/d\theta^2} \right]^{r=a} = \frac{1}{a^2 \theta_1^4} \left[ \frac{(dM_1/dr)^2}{dM_1/d\theta^2 \cdot dM_1/dr} \right]^{r=a} = \frac{1}{a^2 \theta_1^4} \frac{(dM_1/dr)^2}{\int_0^a M_1^2 (a^2 - r^2) r dr} \text{ by 7 (b).}$$

This last expression is essentially positive, since  $r$  is less than  $a$ , hence none of the coefficients in the series (9) can exceed ( $\frac{1}{4}$  — sum of preceding coefficients).

The second proposition is easily proved by a geometrical method, which shows that when  $\theta^2$  is negative  $M_{r=a}$  is a positive quantity greater than unity.

The first few terms in M are

$$M = 1 - \frac{\theta^2 a^2}{4} r^2 + \frac{1}{16} \left( \theta^2 + \frac{\theta^4 a^4}{4} \right) r^4 + \&c.$$

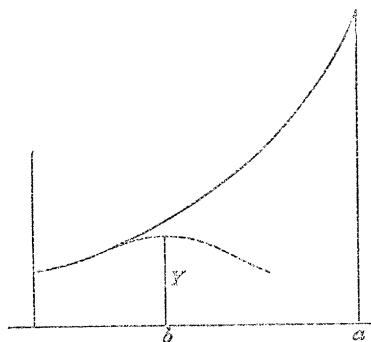
Let us suppose that  $\theta^2$  is negative, and let a curve be drawn, the  $x$  axis of which is  $r$ , and the  $y$  axis M.

When  $x = 0 : y = 1$ ,  $dy/dx = 0$ , and  $d^2y/dx^2$  is positive.

Hence the curve cuts the axis of  $y$  at unit distance from the origin, the tangent to the curve is here parallel to the axis of  $x$ , and as  $x$  increases the tangent begins to slope at a positive angle to the axis of  $x$ ,

From the differential equation of the curve  $x^2 \frac{d^2y}{dx^2} + x \frac{dy}{dx} = -\theta^2 (a^2 - x^2) x^2 y$ , we can easily trace qualitatively the form that the curve takes as  $r$  is increased from 0 to  $a$ .

We have seen that initially, when  $x$  is small,  $y$ ,  $dy/dx$ , and  $d^2y/dx^2$  are positive quantities. Let us suppose that it is possible for  $dy/dx$  to be negative for any value of  $r$  less than  $a$ , the curve taking the form of the dotted line in the figure.



Before  $dy/dx$ , which starts with being positive, can become negative, it must pass through a zero value at  $x = b$ .

The differential equation then gives

$$b^2 \frac{d^2y}{dx^2} = -\theta^2 (a^2 - b^2) b^2 Y.$$

Hence  $d^2y/dx^2$  is positive, therefore as we go along the axis of  $x$  in the positive direction from  $b$ , the tangent to the curve again begins to make a positive angle with the axis of  $x$ , so that  $y$  begins to increase. This shows that  $dy/dx$  cannot be negative at any point between  $x = 0$  and  $x = a$ . Hence the curve must have a form somewhat similar to the continuous line in the figure, the value of  $y$  when  $x = a$  being greater than the value of  $y$  at the origin. Hence the function  $M_{r=a}$  cannot vanish for any negative value of  $\theta^2$ .

7. When  $r$  is made equal to  $a$  in  $M$ , the expression becomes a function of  $\theta^2 a^4$ , with numerical coefficients. The two smallest roots of the equation  $M_{r=a} = 0$  are  $\theta_1^2 a^4 = 7.313$ , and  $\theta_2^2 a^4 = 44.56$ , which were found by expanding the function  $M_{r=a}$  in ascending powers of  $\theta^2 a^4$ . For the determination of these roots, eight terms in the expansion were found; the larger roots cannot conveniently be found by this method, but for the purposes of this investigation their determination is not necessary, as the terms which they introduce into  $R$  are smaller than the experimental errors.

The other numbers which are required are

$$\begin{aligned} \frac{1}{\theta_1^2 a^3} \left[ \frac{dM_1}{dr} \right]_{r=a} &= .1321, & \frac{1}{\theta_2^2 a^3} \left[ \frac{dM_2}{dr} \right]_{r=a} &= .0302, \\ \frac{1}{a^4} \left[ \frac{dM_1}{d\theta^2} \right]_{r=a} &= .0926, & \frac{1}{a^4} \left[ \frac{dM_2}{d\theta^2} \right]_{r=a} &= .0279, \end{aligned}$$

Hence,

$$R = 4 \left[ \frac{.1321}{7.313 \times .0926} e^{-\frac{7.313Kz}{2a^2V}} + \frac{.0302}{44.56 \times .0279} e^{-\frac{44.56Kz}{2a^2V}} + \&c. \right]. \quad (10).$$

This formula holds for gases in general, when the gas which is being absorbed is present in small quantities. This restriction is necessary, since the effect of gravity would disturb the distribution of pressure given in equation (8), especially when the gases A and B differ much in density.

We therefore conclude that, when two gases, A and B, are mixed together and passed along a tube, the surface of which absorbs A, the ratio of the quantity of A which emerges to that which enters is

$$4 \left[ .1952 e^{-\frac{7.313Kz}{2a^2V}} + .0243 e^{-\frac{44.56Kz}{2a^2V}} + \&c. \right],$$

where  $\alpha$  is the radius of the tube,  $z$  its length,  $K$  the coefficient of interdiffusion of the gases A and B, and  $V$  the mean velocity of the gases in the tube.

The effect of the velocity being greater at the centre than at the surface of the tube, is to increase the quantity of A that comes through the tube with B. This can be seen\* by comparing the formula (10) with the function

$$4 \left[ \frac{e^{-\frac{(2.404)^2 Kz}{a^2V}}}{(2.404)^2} + \frac{e^{-\frac{(5.52)^2 Kz}{a^2V}}}{(5.52)^2} + \&c. \right],$$

which is the ratio of the quantity of A coming through the tube to the quantity entering, calculated on the supposition that the velocity of the gases is the same at every point.

If a gas, with ions uniformly distributed in it, has a conductivity  $c_1$  after passing through a tube of length  $l_1$ , and a conductivity  $c_2$  after passing through a tube of length  $l_2$ , we see from Equation (10) that

$$\frac{c_1}{c_2} = \frac{.195e^{-\frac{7.31Kl_1}{2a^2V}} + .024e^{-\frac{44.5Kl_1}{2a^2V}}}{.195e^{-\frac{7.31Kl_2}{2a^2V}} + .024e^{-\frac{44.5Kl_2}{2a^2V}}} \dots \dots \quad (11).$$

8. When the ionization is produced by Röntgen rays the ratio  $c_1/c_2$  can be easily determined for most gases when  $l_1 = 10$  centims.,  $l_2 = 1$  centim.,  $\alpha = 1.5$  millim., and  $V$  about 100 centims. per second. Letting  $c_1/c_2 = y$ , and  $\frac{7.31Kl_1}{2a^2V} = x$ , the values of  $y$  corresponding to a series of values of  $x$  were found, and a curve representing the connection between  $x$  and  $y$  was drawn. The part of this curve which includes the values of  $y$ , which were obtained experimentally, is given in the first diagram, and from it the values of  $\frac{7.31Kl_1}{2a^2V}$  can be immediately found.

\* JOHN S. TOWNSEND, 'Phil. Mag.,' June, 1898.

When hydrogen was passed through the tubing 10 centims. long it was found that its conductivity was so much reduced that it could not be accurately determined. It was therefore necessary to use another apparatus in which  $l_1 = 4$  and  $l_2 = 1$ . The curve showing the connection between  $x$  and  $y$  for the case where  $l_1/l_2 = 4$  is given in the second diagram.

Diagram 1.

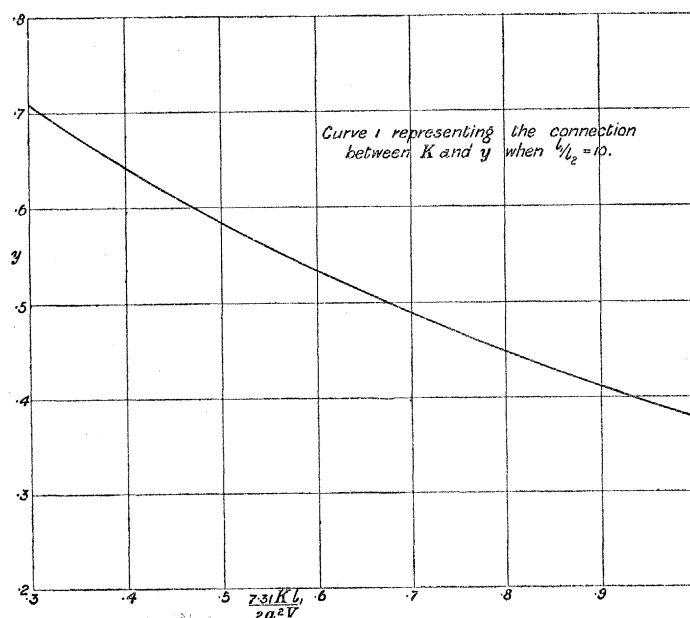
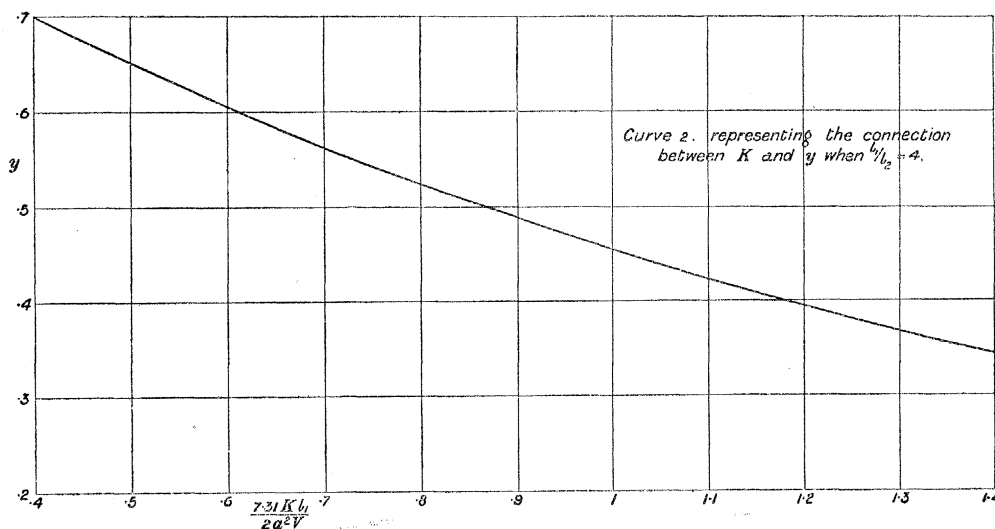


Diagram 2.



## SECTION II.

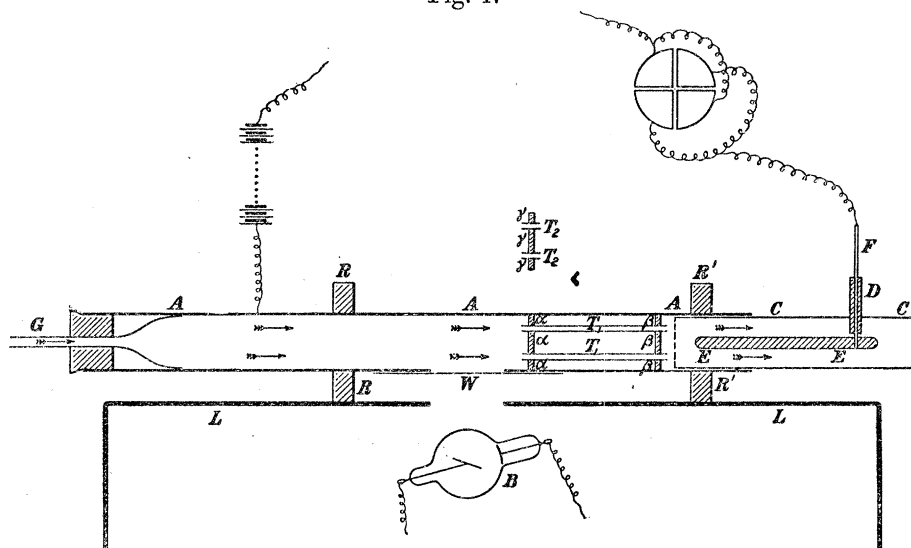
## DESCRIPTION OF APPARATUS.

The apparatus which was used for experiments with air, is shown in fig. 1. It consisted of a brass tube, A, 50 centims. long and 3.2 centims. in diameter, with a

window, *W*, through which the rays from the Crookes tube, *B*, could pass. A second brass tube, *C*, 17 centims. long, fitted tightly into *A*, and could be moved into any desired position. The rod, *F*, to which the electrode, *E*, was fixed, passed through the ebonite plug, *D*, which insulated it from the tube *C*. The electrode, having no other support except *D*, could thus be put into any position in the tube *A* by moving *C*. A series of very fine wires ( $\cdot 1$  millim. in diameter) were soldered parallel to one another, at distances 2 millims. apart, across the end of the tube *C*; the purpose served by this grating will be explained when we come to deal with recombination.

The gas entered the apparatus through the glass tube *G*, and, before reaching the electrode, passed through the tubes *T*. These tubes were soldered into holes bored in two brass discs,  $\alpha$  and  $\beta$ , which fitted exactly into the tube *A*, so that no gas could pass between the discs and the tube. The holes in the discs were equidistant from one another, and lay on a circle whose centre was the centre of the disc. Twelve tubes, 10 centims. long and  $\cdot 3$  centim. in diameter, were thus arranged parallel to one another, two of which are shown in the figure. The symmetry of this arrangement ensured that the velocity along each of the small tubes would be the same. Another twelve tubes, 1 centim. long and  $\cdot 3$  centim. in diameter, were soldered into the disc  $\gamma$ .

Fig. 1.



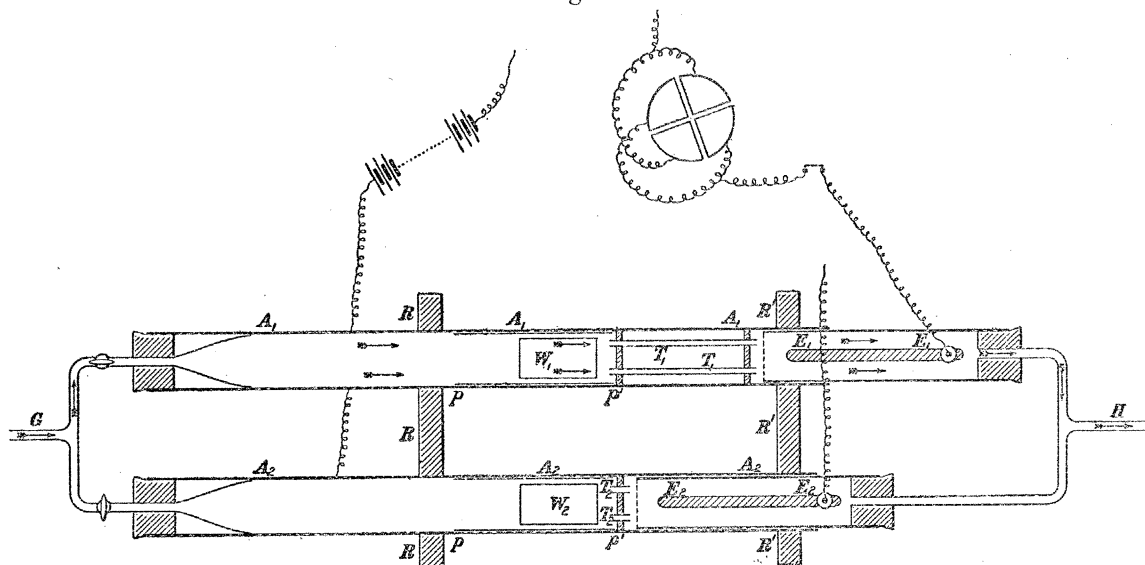
The bulb *B*, and the Ruhmkorff coil with which it was worked, were contained inside a box covered with lead, *L*. A rectangular hole was cut in the box and the lead, through which the rays from the bulb could pass. The lead covering prevented the rays from falling on any other part of the apparatus except the aluminium window *W*, and also screened the wire connecting *F* to the electrometer from electrostatic influence.

The tube *A* was supported by two ebonite rings, *R* and *R'*, which rested on the lead, *L*, and insulated the tube. The potential of the tube was raised to 80 volts by

connecting it to a terminal of a battery of 40 lead cells, the other terminal of which was connected to earth. The electrode, E, was joined to a pair of quadrants of an electrometer, the other quadrants and the case being connected to earth.

In order to obtain a uniform stream of air, the tube, G, was connected to a gasometer, and the velocity of the gas along the tubes, T, could be calculated by observing the rate at which the cylinder of the gasometer fell. When the bulb is giving out rays, the gas, as it passes the aluminium window, becomes a conductor, and the ions are carried with the stream into the tubes  $T_1$ . In passing through these tubes some of the ions are discharged by the sides, and the rest on coming into the field of force (caused by the difference of potential of 80 volts between the electrode and the tube C) are removed from the gas. It will be seen that no external force acts on the ions until they escape from the tubes  $T_1$ , since all parts of the apparatus, except E, are in metallic connection with the large tube A.

Fig. 2.



When the potential of A is positive, the positively charged ions are collected on the electrode, and the deflection of the electrometer needle is proportional to the number of these ions, which come through the small tubes. The negative ions are collected on the electrode by making the potential of A negative.

If the motion of the gas past the electrode were steady, it would only require a difference of potential of a few volts between the electrode and the tube in order to remove all the ions from the gas. This, however, is not the case, since the motion of the gas as it escapes from the tubes, T, is turbulent, so that it is necessary to use a large force in order to get the maximum deflection on the electrometer scale. It was found that when the potential difference was changed from 80 to 40 volts, that the deflections were not appreciably altered; any voltage, therefore, between 40 and 80 would suffice to remove all the ions.

When it was required to find the conductivity of air after passing through short tubes, the tubes  $T_1$  were removed and the disc  $\gamma$  was placed in the position occupied by  $\alpha$ , then the electrode was moved up near the disc so that the electric force should act on the air immediately after leaving the tubes,  $T_2$ .

Experiments with oxygen, hydrogen, and carbonic acid were made with the apparatus, the horizontal section of which is shown in fig. 2. It consisted of two long tubes,  $A_1$  and  $A_2$ , each exactly similar to  $A$  in fig. 1. In one of them the long tubes,  $T_1$ , were set up, and in the other the tubes  $T_2$ . The tubes,  $G$  and  $H$ , were connected to two gasometers, so that the gas could be passed from one to the other, through either of the tubes,  $A_1$  or  $A_2$ . The two tubes were fixed tightly into two rectangular pieces of ebonite,  $R$  and  $R'$ , which rested on the top of the box containing the bulb. Two wooden rails were screwed to the box at such a distance that the ebonite supports fitted exactly between them, so that, by sliding the apparatus from side to side, the window in either of the tubes could be brought exactly over the bulb.

It was found necessary to put a cylinder of aluminium inside each of the tubes, extending from  $p$  to  $p'$ , to prevent the rays from falling on the inner surfaces of the tubes, which were of brass. Before these cylinders were put in experiments were made to see whether the ionization produced in a stream of air passing along  $A_1$  was equal to that produced in an equal stream through  $A_2$ , and it was found that there was a considerable difference between the conductivities in the two cases. The inequality was not due to any difference in the thickness of the aluminium covering the two windows, but was traced to differences in the state of the surfaces of the brass tubes opposite the windows.

It has been shown by PERRIN\* that the ionization produced by Röntgen rays in a gas in contact with a metal is considerably increased by allowing the rays to fall normally on the metal surface. This effect upon the ionization is different for different metals, and depends also upon the state of the surface. According to PERRIN, only a very small increase in conductivity is produced when the rays fall upon an aluminium surface. It was found that, when the two aluminium cylinders were put inside  $A_1$  and  $A_2$ , the difference in conductivity which was first observed disappeared entirely.

#### METHOD OF CONDUCTING THE EXPERIMENTS.

When working with the first form of apparatus the experiments were conducted in the following manner:—The tube  $A$  is raised to a potential of 80 volts positive, and the quadrants to which the electrode is joined are insulated. The stream of air from the gasometer is thus allowed to pass through the apparatus, and, when the velocity is steady, the coil working the bulb is turned on for a fixed time (20 seconds generally) and a deflection of  $n_1$  divisions is obtained on the electrometer scale.

\* 'Comptes Rendus,' vol. 124, p. 455.



The potential of A is then changed to 80 volts negative, and the same experiment is repeated and a negative deflection,  $n'_1$ , is obtained.

The tubes,  $T_1$ , are then removed, and the short tubes,  $T_2$ , are put in their place as already described. Two similar experiments are then made, and larger deflections,  $n_2$  and  $n'_2$ , are obtained when the rays are turned on the same stream of air for the same time.

These four experiments are then repeated several times, and the mean value of the observations is taken in order to eliminate errors arising from variations in the strength of the rays. It was found that the constancy of the bulb was improved by allowing a fixed time (3 minutes) to elapse between each experiment. When this precaution was taken, it was possible to get rays which remained constant within 5 per cent. for the space of an hour.

When working with the second apparatus the numbers  $n_1$  and  $n'_1$  are obtained by sending the gas along the tube  $A_1$ , and finding the deflections when the rays fall on the window,  $W_1$ , for 20 seconds. In order to obtain  $n_2$  and  $n'_2$  it is only necessary to move the apparatus along the top of the box till the window in  $A_2$  comes over the bulb, and to make similar observations with the electrode  $E_2$  joined to the quadrants of the electrometer and the stream of gas passing along  $A_2$ .

#### CORRECTION FOR RECOMBINATION.

Before the coefficients of diffusion can be calculated from the above observations it is necessary to make a correction for the loss of conductivity due to recombination. Let us denote by  $cn$  the number of ions which, when collected on the electrode, give a deflection of  $n$  divisions on the electrometer scale. The above experiments show that there are  $cn_2$  positive ions which pass the section of the tubes,  $T_1$ , at a distance of 1 centim. from the end near the window,  $W_1$ . Of these  $cn_2$  ions  $c(n_2 - n_1)$  are lost in the remaining 9 centims. of the tubes. The loss is principally due to the ions coming into contact with the sides of the tubes; but the loss is also to a small extent due to collisions between positive and negative ions; it is necessary to find how much the observed value of  $n_1$  must be increased in order to compensate for the loss of ions arising from recombination. If  $cM$  is the number of positive ions which encounter negative ions and do not come into contact with the sides, then the ratio  $\frac{n_1 + M}{n_2} = y$  is the number which is required in order to calculate the coefficient of diffusion from the curve given in Section I. Recombination also takes place in the short tubes  $T_2$ , but this effect is too small to take into account.

In order to find  $M$  it is necessary to find the rate at which the gas loses conductivity due to recombination, and this can be easily done by making a change in the arrangement of the apparatus. The tubes  $T_1$  and  $T_2$  were removed from  $A_1$  and  $A_2$ , and the electrodes were placed in the positions shown in fig. 2, the wire grating in front of the electrode  $E_1$  being 12 centims. from the window in  $A_1$ , and the grating in

front of  $E_2$  3 centims. from the window in  $A_2$ . The gratings in front of the electrodes, being in metallic connection with the tubes  $A_1$  and  $A_2$ , prevent the fields of force from extending up the tubes, so that when ions are produced in a stream of gas they are not acted upon by any force till they cross the grating.

A stream of gas is passed through the tube  $A_1$  and the rays allowed to fall upon it for 20 seconds. The positive ions are collected on the electrode as before, and a deflection  $N_1$  is obtained on the electrometer scale (it is not necessary in this case to make a similar experiment with the negative ions). The apparatus is then moved so as to bring the window  $W_2$  over the bulb, and the stream of gas is sent through the tube  $A_2$ , and the deflection  $N_2$ , which is greater than  $N_1$ , is obtained when the same experiment is made with the electrode  $E_2$  joined to the electrometer. If  $d_1$  and  $d_2$  are the distances of the gratings from the windows  $W_1$  and  $W_2$ , we see that the conductivity falls from  $N_2$  to  $N_1$ , while the gas travels the distance  $(d_1 - d_2)$ . This reduction in conductivity is nearly entirely due to recombination, since the tubing is so wide that the loss due to diffusion to the sides is inappreciable. The mean time  $T$  that the gas takes to traverse the distance  $d_1 - d_2$  can be found from the rate at which the gas escapes from the gasometer. It is important that this rate of escape should be the same as the rate of escape in the experiments in which  $n_1$  and  $n_2$  were determined, so that the ions should be distributed throughout the same volume of gas.

If  $cN$  is the number of ions in a gas in which no new ions are being produced, then the rate at which  $N$  varies with the time is given by the formula :

$$dN/dt = - aN^2, *$$

when no other influences except recombination contribute to the reduction in  $N$ .

Hence, by integration,

$$\frac{1}{N_1} - \frac{1}{N_2} = \alpha T,$$

where  $T$  is the time in which the conductivity falls from  $N_2$  to  $N_1$  due to recombination. The value of  $\alpha$  can therefore be determined by substituting the observed values of  $N_1$ ,  $N_2$ , and  $T$  in this equation.

Returning to the case where the gas passes along the fine tubes, the conductivity falls from  $n_2$  to  $n_1$  while the gas passes along the last nine centims. of  $T_1$ . Let  $\theta$  be the average time that any portion of the gas takes to traverse these nine centims. The amount of ionization per cub. centim. of gas can easily be reduced so that the loss of conductivity due to recombination is only  $\frac{1}{20}$ th of that due to diffusion to the sides.

From formula 10, Section I., we see that the conductivity  $n$  at any section of the tubes  $T_1$  is given approximately by the formula :

\* J. J. THOMSON and RUTHERFORD, 'Phil. Mag.,' November, 1896.

$$n = n_2 e^{-\beta t},$$

where  $t$  is the time occupied by the gas in travelling from the section where its conductivity is  $n_2$  to the section where its conductivity is  $n$ .

From observation we have :

$$n_1 = n_2 e^{-\beta \theta},$$

so that

$$\beta = \frac{1}{\theta} \log \frac{n_2}{n_1}.$$

Let  $cp$  be the number of positive ions which recombine with negative ions in the tubes  $T_1$ . Then

$$dp/dt = \alpha n^2 = \alpha n_2^2 e^{-2\beta t},$$

and  $p = 0$  when  $t = 0$ .

Let  $P$  be the value of  $p$  at the end of the tubes, the value of  $t$  being  $\theta$  at that point.

By integration we obtain :

$$P = \alpha \frac{n_2^2 - n_1^2}{2\beta} = \alpha \theta \frac{n_2^2 - n_1^2}{2 \log \frac{n_2}{n_1}}.$$

Substituting for  $\alpha$  its value this equation becomes

$$P = \frac{\theta}{T} \cdot \frac{n_2^2 - n_1^2}{2 \log \frac{n_2}{n_1}} \cdot \frac{N_2 - N_1}{N_1 N_2}.$$

The effect of recombination would obviously be over-corrected for if  $M$  were taken equal to  $P$ , for although  $cP$  ions are lost by encounters with others of opposite sign, still it must be remembered that, had no recombination taken place, some of these  $cP$  ions would have lost their charge to the sides of the tube. The number  $cM$  should only include those ions which encounter others of opposite sign, and would not subsequently come into contact with the sides if their rate of diffusion were unaltered by the collisions.

It is easy to see that  $M$  is less than  $P$  and greater than  $\frac{n_1}{n_2} P$ ; a fairly accurate estimation of its value can be arrived at by the following method :—

At a section  $z$  of the tubes, where the conductivity is  $n$ , the number that recombine in a time  $dt$  is  $cdp$ , where  $dp = \alpha n^2 dt$ .

From the formula 10, Section I., it can be seen that of these  $c\delta p$  ions,  $c\delta p \frac{n_1}{n}$  would not come into contact with the sides as they pass from  $z$  to the end of the tubes  $T_1$ , if their rate of diffusion were unaltered by the recombination. Hence we have

$$\delta M = \delta p \frac{n_1}{n} = \alpha n n_1 \delta t = \alpha n_1 n_2 e^{-\beta t} \delta t.$$

We therefore obtain, by integration from  $t = 0$  to  $t = \theta$ ,

$$M = \frac{\alpha n_1 n_2 (1 - e^{-\beta\theta})}{\beta} = \frac{\alpha n_1 (n_2 - n_1)}{\beta}.$$

Substituting for  $\alpha$  and  $\beta$  their values, this equation becomes

$$M = \frac{N_2 - N_1}{N_1 N_2} \times \frac{\theta}{T} \cdot \frac{n_1 (n_2 - n_1)}{\log \frac{n_2}{n_1}}.$$

#### CHARGE ACQUIRED BY THE GAS.

The deflections  $n_1$ , which are obtained by collecting the positive ions after the gas has passed through the long tubes  $T_1$ , are invariably greater than the corresponding negative deflections  $n_1'$ , which shows that the gas on issuing from the tubes  $T_1$  has a positive charge proportional to  $n_1 - n_1'$ . In each of the tubes  $T_1$  there is a small force arising from this charge, which repels the positive ions towards the sides and attracts the negative ions towards the axes of the tubes. It is only when the rays are strong that this force has any appreciable effect on the motion of the ions.

The deflections  $n_2$  are also slightly greater than  $n_2'$ , but the difference between these numbers is not so great as the difference between  $n_1$  and  $n_1'$ . The values which are obtained for the ratios  $\frac{n_1 + M}{n_2}$  are greater than the corresponding values of  $\frac{n_1' + M}{n_2'}$ , which shows that the negative ions diffuse faster than the positive ions.\*

It was found that the rates of diffusion of the positive and negative ions differed more when the gases were dry than when they were moist. Two sets of experiments were therefore made with each gas; in one set the gas was passed through large tubes of calcium chloride and entered the diffusion apparatus dry; in the other set the calcium chloride tubes were removed, and long tubes, partly filled with water, were put in their place. In all the experiments the gases passed through plugs of glass wool before entering the tubes A, in order to remove any dust that might be present.

#### RESULTS OF EXPERIMENTS WITH AIR.

The following tables give the numbers  $n_1$ ,  $n_1'$ ,  $n_2$ , and  $n_2'$ , which were obtained with different strengths of rays. The intensity of ionization was reduced to any required value by covering the hole in the lead with pieces of aluminium or zinc. Each experiment consists in determining the four electrometer deflections with a constant strength of rays. The positive and negative deflections  $n_1$  and  $n_1'$  are given in the same column, the number in the upper line being  $n_1$  and that in the lower  $n_1'$ . The corresponding observations  $n_2$  and  $n_2'$  are arranged in a similar manner in the next

\* J. ZELENY, 'Phil. Mag.,' July, 1898, describes an experiment to which he gives a similar interpretation.

column.  $M$  is the correction for recombination, which has to be added to  $n_1$  and  $n_1'$  in order to obtain the ratios  $\frac{n_1 + M}{n_2}$  and  $\frac{n_1' + M}{n_2'}$ , which are the required values of  $y$ . The values of  $\frac{7.31K \times 10}{2a^2V}$  are deduced from Curve I., Section I.;  $a^2V$ , the square of the radius of the tubing  $T$  multiplied by the velocity of the gas, is obtained by observing the rate of escape of the gas from the gasometer. The coefficients of diffusion of the ions into the gas are given in the last column.

Table I. gives the results of experiments with dry air, and Table II. the results obtained with moist air.

TABLE I. for Dry Air.

Experiment.	$n_1$ and $n_1'$ .	$n_2$ and $n_2'$ .	$M$ .	$y$ .	$\frac{7.31K}{2a^2V}$ .	$a^2V$ .	$K$ .
I.	+	18.6	32.5	.5	.588	2.06	.028
	-	13.0	29.1		.464		.043
II.	+	63.6	118	4.0	.573	2.06	.0296
	-	50.1	110		.491		.0395
III.	+	128	262	22.0	.572	2.06	.0296
	-	104	244		.516		.038
Mean . . . . .							.0346

We see that, as the strength of the rays is increased, the values of  $K$  for the positive ions appear to increase, and the values for the negative ions to diminish. It will be observed that the charge on the gas ( $n_1 - n_1'$ ) varies from 5.6 to 24, and, as already explained, this charge acts in such a manner as to make the calculated value of  $K$  for the positive ions too big and that for the negative ions too small. The nearest value for the ratio of the coefficients of diffusion is therefore 1.54, as given by the first experiment.

Experiments were made to see whether consistent results would be obtained by varying the velocity  $V$ , and .036 was obtained for the mean value of  $K$  when  $a^2V$  was 1.57.

An experiment with air, made with the apparatus arranged for the other gases, gave the mean value of  $K = .034$ .

These values are as consistent as could be expected when all possible sources of error are taken into account.

TABLE II. for Moist Air.

Experiment.	$n_1$ and $n_1'$ .	$n_2$ and $n_2'$ .	M.	$y$ .	$\frac{73 \cdot 1 K}{2a^2 V}$ .	$a^2 V$ .	K.
I.	+	23·3	1·0	·563	·54	2·12	·031
	-	20·3		·532	·61		·035
II.	+	57·0	4·0	·542	·585	2·06	·033
	-	51·0		·515	·464		·036
III.	+	122·4	24·0	·559	·58	2·11	·032
	-	112		·546	·55		·035
Mean . . . .							·0335

These results show that the mean rate of diffusion is only slightly altered by the presence of moisture, but a large change is produced in the ratio of the coefficients of diffusion of positive and negative ions.

An experiment made with the apparatus shown in fig. 2 gave ·034 for the mean value of K.

#### *Oxygen.*

The oxygen which was used was taken from a cylinder which contained about 94 per cent. of oxygen, the other 6 per cent. being principally nitrogen. The rates of diffusion of the ions through oxygen and air only differ by about 5 per cent., so that the presence of 10 per cent. of air would only increase the rate of diffusion by ·5 per cent. No correction need therefore be made for the presence of nitrogen in the gas.

The experiments on diffusion gave results exactly similar to those obtained with air, except that the values of K were about 6 per cent. smaller.

The coefficients of diffusion which were obtained for positive and negative ions in dry oxygen are ·025 and ·0396 (mean ·0323).

The corresponding numbers for the moist gas are ·0288 and ·0358 (mean ·0323).

#### *Carbonic Acid.*

The carbonic acid which was used was taken from a cylinder. As in the case of oxygen, no correction need be made for the presence of a few per cent. of air mixed

with the gas. It would require 3 per cent. of air to make a difference of 1 per cent. in the coefficient of diffusion of the ions into carbonic acid

The coefficients of diffusion which were obtained for the positive and negative ions in the dry gas are  $\cdot 023$  and  $\cdot 026$ .

The corresponding numbers for the moist gas are  $\cdot 0245$  and  $\cdot 0255$ .

The most remarkable difference between the diffusion in carbonic acid and other gases is that the rate of diffusion is nearly equal for the positive and negative ions. In oxygen, air, and hydrogen the rates of diffusion of the positive and negative ions differ by as much as 50 per cent. when the gases are dry, whereas in carbonic acid the difference amounts only to 12 per cent.

### *Hydrogen.*

The hydrogen which was used was generated by the action of hydrochloric acid on zinc. The gas was bubbled through three strong solutions of caustic potash and potassium permanganate, in order to remove the acid vapour and the hydrocarbons, and collected in one of the gasometers. The purity of the gas was tested by finding its specific gravity, which is a very sensitive method of detecting the presence of other gases in hydrogen, since the density of the latter is so small. For this purpose a glass flask having a capacity of about 500 cub. centims. was used. Its volume was accurately found, and its loss of weight when dry hydrogen was substituted in it for dry air; from these two measurements the specific gravity of the gas could be calculated.

The presence of 1 per cent., by pressure, of air would alter the density by 14.5 per cent., which can be very easily detected, as 1 per cent. of air in a 500 cub. centim. flask weighs about 6 milligrammes. It was found that the specific gravity of the hydrogen which was prepared did not differ by 2 per cent. from the value  $\cdot 00009$ . After being in the gasometers and the diffusion apparatus for a few days the gas rose in density, due to air getting in. It would have been a matter of great difficulty to have made an apparatus, which had so many rubber joints, perfectly gas-tight, and it was considered simpler to find the amount of air in the hydrogen after each experiment, and to make a correction in the observed coefficient of diffusion.

We may here mention an experiment made with the same apparatus as was used for the determination of the rates of diffusion of the ions into oxygen and carbonic acid. The same velocity of gas in the tubing T was used,  $\alpha^2V$  being 2.08. The positive and negative deflections obtained after the gas had passed through the tubes  $T_2$  were 29 and 27.5, and the deflections after passing through the tubes  $T_1$  were 6.5 and 2.2. This shows that in the last nine centimetres of the tubes  $T_1$  the mean conductivity of the hydrogen fell from 28.2 to 4.3. An experiment with oxygen made with the same velocity,  $\alpha^2V = 2.08$ , showed that the mean conductivity of oxygen was reduced from 30.8 to 15.8. The difference in the behaviour of the ions

in the two gases cannot be attributed to a greater rate of recombination of ions in hydrogen, as other experiments show that the ions in hydrogen recombine somewhat slower than the ions in oxygen.

Another set of 12 tubes were therefore made, 4 centims. long, and of the same diameter as the tubes  $T_1$ , and substituted in the apparatus shown in fig. 2 instead of the tubes  $T_1$ . A series of experiments were made, and values of  $\gamma$  were obtained which gave the ratios of the conductivities after the gas had passed through tubing 4 centims. and 1 centim. in length. The corresponding values of  $K$  were obtained from Curve II., Section I. In correcting for recombination in these experiments it is necessary to take into account the recombination in the tubes 1 centim. long.

The results obtained from experiments with dry hydrogen which contained 1·6 per cent. of air, are :

$$K = \cdot 117 \text{ for the positive ions,}$$

and

$$K = \cdot 181 \text{ for the negative ions.}$$

The coefficients of diffusion in a mixture containing 1·8 per cent. of air, 1·5 per cent. of water vapour, and 96·7 per cent. of hydrogen are : ·121 and ·134 for the positive and negative ions.

These results show that the rates of diffusion in hydrogen are 4·3 times as great as the rates of diffusion in air. In order, therefore, to obtain the coefficients of diffusion in pure hydrogen at atmospheric pressure, the above determinations must be increased by 3·3 per cent. for each per cent. of air in the gas.

Applying this correction, we obtain the following values for the coefficients of diffusion of the ions into hydrogen :

$$K = \cdot 123 \text{ for positive ions in dry hydrogen,}$$

and

$$K = \cdot 190 \text{ for negative ions in dry hydrogen.}$$

The corresponding coefficients for moist hydrogen are :

$$K = \cdot 128 \text{ for positive ions,}$$

and

$$K = \cdot 142 \text{ for negative ions.}$$

The coefficients of diffusion for the four gases which were examined are given in the following tables.

TABLE III.—Coefficients of diffusion of ions in dry gases.

Gas.	K for + ions.	K for - ions.	Mean value of K.	Ratio of the values of K.
Air . . . . .	·028	·043	·0347	1·54
Oxygen . . . . .	·025	·0396	·0323	1·58
Carbonic acid . . . . .	·023	·026	·0245	1·13
Hydrogen . . . . .	·123	·190	·156	1·54



TABLE IV.—Coefficients of diffusion of ions in moist gases.

Gas.	K for + ions.	K for - ions.	Mean value of K.	Ratio of the values of K.
Air . . . . .	·032	·035	·0335	1·09
Oxygen . . . . .	·0288	·0358	·0323	1·24
Carbonic acid . . . . .	·0245	·0255	·025	1·04
Hydrogen . . . . .	·128	·142	·135	1·11

## REMARKS ON THE EXPERIMENTS.

The values of  $y$  which were found in these experiments are probably correct to 3 per cent., but on referring to the curves it will be seen that the error in  $K$  is larger than the error in  $y$ . For example, considering Curve I. at the point  $y = \cdot 5$ , it will be seen that a 4 per cent. error in  $y$  gives rise to a 6 per cent. error in  $K$ . We would therefore expect that the values of  $K$  are correct to about 5 per cent. In order to diminish  $y$  without changing the apparatus, the velocity of the gas in the tubing has to be diminished, and this has the effect of increasing in importance the correction for recombination. It was therefore considered best to use velocities of the blast which give  $y$  about  $\cdot 5$ .

It has been assumed that the velocity of the gas is given by the formula  $W = \frac{2V}{\alpha^2}(\alpha^2 - r^2)$ , and that the motion takes place in straight lines parallel to the axis of the tube. According to Professor REYNOLDS, the motion of a fluid in a tube is not in straight lines when the velocity exceeds a certain critical value, and eddies are produced even when the motion is initially in lines parallel to the axis. When the velocity is less than another critical velocity, any irregular motion will tend to return to the straight line motion. In order to ensure that the motion of any fluid, whose density is  $\rho$ , and viscosity  $\mu$ , should tend to be in straight lines and obey the formula  $W = \frac{2V}{\alpha^2}(\alpha^2 - r^2)$ , the value of  $V\rho\alpha/\mu$  must be less than 700.

In the present experiments  $V\rho\alpha/\mu$  is less than 100, so that the velocities used are  $\frac{1}{7}$  of the second critical velocity.

## THE ATOMIC CHARGE.

The most interesting results which can be deduced from the coefficients of diffusion are obtained by comparing the velocity under an electromotive force with the coefficient of diffusion.

Considering one of the equations of motion

$$\frac{1}{K} pu = - \frac{dp}{dx} + nXe,$$

where  $e$  is the charge on the ion of the gas in electrostatic units,  $n$  the number of ions per cub. centim., and  $p$  their partial pressure, we see that when  $dp/dx = 0$ , the velocity  $u$  due to the electric force  $X$  is  $\frac{nXeK}{p}$ . If the potential gradient is 1 volt per centim.,  $X = \frac{1}{300}$  in electrostatic units, and the corresponding value of  $u$  is

$$u_1 = \frac{Ke}{300} \times \frac{n}{p}.$$

Let  $N$  be the number of molecules in a cub. centim. of a gas at pressure  $P$ , equal to the atmospheric pressure, and temperature  $15^\circ$  Centigrade, the temperature at which  $u_1$  and  $K$  are determined.

The quotient  $N/P$  may be substituted for  $n/p$  in the above equation, and since the atmospheric pressure  $P$  in C.G.S. units is  $10^6$ , we obtain

$$Ne = \frac{3 \times 10^8 u_1}{K}.$$

If we take the values of  $u_1$  from the table of mean velocities given by RUTHERFORD,\* and the mean values of  $K$  obtained for dry gases, we get the following values of  $Ne$  :—

Air . . . . .	$Ne_A = 1.35 \times 10^{10}$ ,
Oxygen . . . . .	$Ne_O = 1.25 \times 10^{10}$ ,
Carbonic acid . . . . .	$Ne_C = 1.30 \times 10^{10}$ ,
Hydrogen . . . . .	$Ne_H = 1.00 \times 10^{10}$ ,

Experiments on electrolysis show that 1 electrodynamic unit of electricity in passing through an electrolyte gives off 1.23 cub. centims. of hydrogen at temperature  $15^\circ$  Centigrade and pressure =  $10^6$  C.G.S. units. The number of atoms in this volume is  $2.46 N$ , so that if  $E$  is the charge on a hydrogen atom in the liquid electrolyte,

$$\begin{aligned} 2.46 NE &= 1 \text{ electromagnetic unit,} \\ &= 3 \times 10^{10} \text{ electrostatic units.} \end{aligned}$$

Hence

$$NE = 1.22 \times 10^{10},$$

the charge  $E$  being expressed in electrostatic units.

Since  $N$  is a constant, we conclude that the charges on the ions produced by Röntgen rays in air, oxygen, carbonic acid, and hydrogen are all the same, and equal to the charge on the hydrogen ion in a liquid electrolyte.

Professor THOMSON† has shown that the charge on the ions in hydrogen and oxygen, which have been made conductors by Röntgen rays, is  $6 \times 10^{-10}$  electrostatic unit, and is the same for both gases.

\* E. RUTHERFORD, 'Phil. Mag.,' November, 1897.

† J. J. THOMSON, 'Phil. Mag.,' December, 1898.

Taking this value for the charge  $e$ , we obtain

$$N = 2 \times 10^{19}.$$

From this we deduce the weight of a molecule of hydrogen

$$4.5 \times 10^{-24} \text{ gramme.}$$

Every step in the theory by which these numbers are obtained is supported by direct experimental evidence.

Since, as we have just shown, the charge on an ion produced by Röntgen rays, is equal to the charge on a hydrogen ion in a liquid electrolyte, this latter charge is also  $6 \times 10^{-10}$  electrostatic unit.

Although the value of  $Ne$  for hydrogen is 25 per cent. different from its value for other gases, we are justified in including hydrogen in the above general conclusion, as we would expect the value of  $u_1$  for hydrogen to be too small. RUTHERFORD makes no mention of having corrected for the presence of air in his apparatus, or of having used perfectly dry hydrogen. If we take the mean value of  $K$  for moist hydrogen, we obtain

$$Ne_H = 1.15 \times 10^{-10}.$$

In order to prove that the charge on the positive ion is equal to the charge on the negative ion, the ratio of the coefficients of diffusion must be shown to be equal to the ratio of the velocities. Professor ZELENY\* has shown that the negative ions travel faster under an electromotive force than the positive ions, the ratio of the velocities being 1.24 for air and oxygen, 1.15 for hydrogen, and 1.0 for carbonic acid.

The experiments on diffusion show that the ratio of the velocities would be larger in dry than in moist gases, but as this point has not yet been examined by Professor ZELENY, we cannot expect a very close agreement between the ratios which he gives for the velocities and the ratios of the coefficients of diffusion.

We are led to conclude that the charges on the positive and negative ions are equal from another point of view. It has been proved that the mean charge is the same as the charge on an ion of hydrogen in a liquid electrolyte. If the charges differed, one of them would be less than the charge on the hydrogen ion, whereas experiments on electrolysis show that all ionic charges are either equal to the charge on the hydrogen ion, or an exact multiple of it.

#### COMPARISON OF THE RATES OF DIFFUSION OF THE IONS WITH THE RATES OF INTERDIFFUSION OF GASES AND VAPOURS.

The coefficients of diffusion of ions into a gas are much smaller than the coefficients

\* J. ZELENY, 'Phil. Mag.,' July, 1898.

of diffusion of gases into each other, but do not differ much from the coefficients of diffusion of vapours into gases.

We give here a table of the latter coefficients, so that they may be compared with the numbers given in Tables III. and IV.

TABLE V., giving Coefficients of Diffusion of some Gases and Vapours into Air, Carbonic Acid, and Hydrogen.

Gas or vapour.	Air.	Carbonic acid.	Hydrogen.	Observer.
Oxygen . . . . .	...	·18	·721	LOSCHMIDT
Carbonic acid . . . . .	·142	...	·555	
Æther . . . . .	·077	·055	·29	WINKELMANN
Alcohol . . . . .	·101	·068	·378	
Water . . . . .	·198	·132	·687	

The experimental results show that if  $K$  is the coefficient of interdiffusion of two gases whose densities are  $\rho_1$  and  $\rho_2$ ,  $K \times \sqrt{\rho_1 \rho_2}$  is roughly constant. The rates of diffusion of the ions are roughly inversely proportional to the square roots of the densities of the gases.

Two theories have been suggested to account for the small values which have been found for the rates of diffusion of the ions into a gas.

The effect may be explained if we suppose that a number of molecules surround the ion. The carriers of the charge would then diffuse slowly like a gas made up of large molecules. The mass of the group could be found by comparing the rates of diffusion of the ions with the rates of interdiffusion of gases. A rough calculation shows that the mass of this group should be about 30 times the mass of a molecule of oxygen.

The small values of the coefficients of diffusion may also be explained if we suppose that the carrier is as small as a molecule of the gas, and that the electric force exerted on the molecules which approach it gives rise to encounters which would not have taken place if the carrier were uncharged.

If we adopt the theory that the ions are surrounded by molecules forming a sphere which moves about with the ion, we can apply MAXWELL'S formula for the coefficient of interdiffusion of two gases to find the radius of the sphere.

The coefficient of interdiffusion of two gases, according to the theory founded on the collisions of elastic spheres, is

$$D_{12} = \frac{1}{2\sqrt{6\pi}} \cdot \frac{V}{N} \cdot \sqrt{\frac{1}{w_1} + \frac{1}{w_2}} \cdot \frac{1}{S_{12}^2} *$$

where  $w_1$  and  $w_2$  are the molecular weights of the two gases, that of hydrogen being unity.

\* J. C. MAXWELL, 'Nature,' vol. 8.

$S_{12}$  is the distance between the centres of the molecules at collision in centimetres.

$V$  is the "velocity of mean square" of a molecule of hydrogen at  $0^\circ$  C.

$$V = \sqrt{(3p/\rho)} = 186000 \text{ centims. per second.}$$

$N$  is the number of molecules in a cubic centimetre at  $0^\circ$  and 760 millims. pressure.

Taking the value of  $N$ , which we have found,  $2 \times 10^{19}$ , we see that

$$D_{12} = 1.1 \times 10^{-15} \sqrt{\left(\frac{1}{w_1} + \frac{1}{w_2}\right) \frac{1}{S_{12}^2}}$$

If the carrier of the charge is large compared with the molecule,  $S_{12}$  will be the radius of the carrier and  $1/w_2$  will be small compared with  $1/w_1$ .

Letting  $D_{12} = .156$ , the coefficient of diffusion of ions into hydrogen,  $w_1 = 1$ , we obtain for the radius of the ion in hydrogen

$$S = \sqrt{\frac{1.1 \cdot 10^{-15}}{.156}} = 8.2 \times 10^{-8}.$$

A similar calculation shows that the radius of an ion in oxygen is

$$9.2 \times 10^{-8}.$$

Adopting the second theory which we have proposed to account for the slowness of the rates of diffusion of the ions, and applying the same formulæ, the values of  $S$  will be greater than the above values by the factor  $\sqrt{2}$ , since the terms  $1/w_1$  and  $1/w_2$  are of the same order.

The values obtained in this way for  $S_{12}$  would denote the distance that a molecule of the gas must approach an ion in order that the electric force should appreciably alter its motion.

#### RECOMBINATION.

The results of the experiments which were made to determine the rate of recombination are given in the following table.  $T$  is the time, in seconds, in which the conductivity falls from  $N_2$  to  $N_1$ , and  $V$  is the volume, in cub. centims., of gas which was used in each experiment.

TABLE VI.

Gas.	$N_2$ .	$N_1$ .	$T$ .	$V$ .	Correction to be added to $N_1$ .
Air . . . . .	77	43	.93	1540	3
Oxygen . . . . .	59.5	37	.95	1520	2
Carbonic acid. . . . .	62.5	39	.90	1590	2
Hydrogen . . . . .	117	85	.275	1360	5

The numbers  $N_1$  and  $N_2$  are the electrometer deflections obtained in the manner described above. In the first three gases the electrode  $E_1$  was at a distance 12 centims. from the window  $W_1$ , and the electrode  $E_2$  at a distance 3 centims. from the window  $W_2$ . The conductivity therefore fell from  $N_2$  to  $N_1$  while the gas passed through 9 centims. of the tube  $A_1$ .

The position of the electrodes had to be altered for hydrogen, as this gas would have lost about 16 per cent. of its conductivity, due to diffusion to the sides alone, in passing along 9 centims. of the wide tubing. The electrodes were therefore put at distances 3 and 6 centims. from the windows, and the strength of the ionization was increased.

The correction given in the tables is to compensate for the loss of conductivity arising from diffusion.

The electrometer was standardised, and it was found that each division corresponded to a charge of  $\cdot 0042$  electrostatic unit. If  $e$  is the charge on the ion, the number of ions in a cub. centim. is  $\frac{N \times \cdot 0042}{eV}$ , which we will denote by  $v$ .

From the theory of recombination we have

$$dv/dt = \beta v^2, \quad \text{or} \quad \frac{1}{v_2} - \frac{1}{v_1} = \beta T.$$

From the numbers given in Table VI. we can obtain the values of  $\beta$  for the different gases. We thus find that for air, oxygen, carbonic acid, and hydrogen the values of  $\beta$  are,  $3420 \times e$ ,  $3380 \times e$ ,  $3500 \times e$ , and  $3020 \times e$ .

The rates of recombination in air, oxygen, and carbonic acid are practically the same, and about 15 per cent. greater than the recombination in hydrogen.

Substituting for  $e$  its value, we obtain for the first three gases  $\beta = 2 \times 10^{-6}$ , *q.p.*

We can now find how near two ions of opposite sign must approach each other in order to recombine. If there are  $v$  positive ions, and  $v'$  negative ions, in a cub. centim., the number that recombine in a time  $\delta t$  is  $vv'\beta\delta t$ .

The number of negative ions that approach within a distance  $S$  of positive ions in the same time can be found from the kinetic theory of gases.

MAXWELL has shown\* how to calculate the number of times per second a molecule of one gas will come within a distance  $R$  of the molecules of another gas.

This number is

$$2n \sqrt{\pi} \sqrt{(\alpha^2 + \beta^2)} R^2,$$

where  $n$  is the number of molecules per cub. centim. of the second gas,  $\alpha^2 = \frac{2}{3} v_1^2$ ,  $\beta^2 = \frac{2}{3} v_2^2$ ,  $v_1^2$  and  $v_2^2$  are the mean squares of the velocities of agitation of the two gases.

We will suppose that an ion has the same mass as a molecule of the gas in which

\* 'Phil. Mag.,' January and July, 1860.

it is produced. The mean square of the velocity of agitation of the ions will, on this hypothesis, be equal to the mean square of the velocity of agitation of the molecules of the gas.  $v_1^2$  and  $v_2^2$  will then be equal to  $4.7 \times 10^4$  for the ions in oxygen.

The number of negative ions that approach within a distance  $R$  of positive ions in the time  $\delta t$  will be

$$2vv' \sqrt{\pi} \sqrt{\frac{2}{3} (v_1^2 + v_2^2)} R^2 \delta t.$$

Equating this number to the number that recombine in the same time we obtain

$$R = \frac{1}{3} 10^{-5} \text{ centim.}$$

At a distance  $\frac{1}{3} 10^{-5}$  the charge on an ion would exert a force equal to a fall of potential of 16,200 volts. per centim. This force would make two oppositely-charged ions move towards each other with a velocity of  $2 \times 10^4$  centims. a second.

It would be premature to discuss any further the results which have been obtained, as experiments are being carried out which may throw additional light upon the subject.

In conclusion, I wish to state that I am greatly indebted to Professor THOMSON for his advice and suggestions during the course of these investigations.