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XXXVI. Ionization by collision

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become impaired. In that case it can, if desired, be restored by the use of an objective cylindrical lens (§ 22).

The method of detecting and measuring small angular displacements, which forms the subject of this paper, was developed in connexion with a "search for a new property of matter in motion," for which a grant was obtained through the Royal Society. I have also to thank the Earl of Berkeley for most kindly placing the resources of his laboratory workshop at my disposal.

Boars Hill, Oxford.

Nov. 1911.

XXXVI. *Ionization by Collision.*

By NORMAN CAMPBELL, *Sc.D.**

1. **T**HE theory of ionization by collision of ions and the application of it to explain the electrical discharge through gases at low pressures is due mainly to Townsend†. In the course of some recent work, described in the following paper, doubts have been thrown upon the accuracy of the mathematical argument by which his formulæ are derived from his physical assumptions. Those assumptions are not doubted, but since some of them are of sufficient interest to merit special consideration, Townsend's entire argument will be sketched briefly.

2. Townsend makes the following hypotheses:—

(1) An ion, positive or negative, formed by any means in a gas, will produce a fresh pair of ions when it collides with a neutral molecule, if previously to that collision it has fallen freely under the action of the electric field through a potential not less than some finite value V' . V' is much greater for positive than for negative ions. In what follows negative ions only will be under consideration, for it will be assumed that the electric fields are so small that there is no appreciable ionization by collision of the positive ions.

(2) An ion, after collision with a neutral molecule, whether or not that collision results in the production of fresh ions, retains no portion of its previous velocity, but starts again from rest; it retains, however, its charge. (The velocity of thermal agitation is so small compared with that acquired under the action of the field in all the cases considered that it may be neglected.)

* Communicated by the Author.

† Townsend's work in this direction is summarized in his volume 'The Theory of the Ionization of Gases by Collision' (Constable, London, 1910. References will be made throughout to this book),

(3) An ion, however formed, immediately after its formation has a velocity so small that it may be neglected.

(4) A collision, whether or not it results in ionization, does not change the nature of the ion in such a way that it is incapable of ionization at subsequent collisions after a free fall through the potential difference V' .

3. Assumption (1) is the basis of the theory. (2) is almost certainly not accurately true; an ion after collision retains some portion of its previous velocity; but the assumption is made for simplicity of calculation. The error probably does not lead to an error in the form of the formulæ deduced, but only to values of N or V' which are somewhat too small. (3) is considered at length in the following paper* on "Ionization by α rays."

(4) is deserving of further consideration. When the theory of gaseous ionization was first advanced by Thomson and Rutherford, it was believed that the negative ion consisted of a group of several molecules collected round an electron. Ionization was thought to consist in the liberation of an electron from a neutral molecule, the collection of other neutral molecules round it being effected at subsequent collisions. If this view, already considerably discredited, were correct, a negative ion immediately after its formation would be a system different from a negative ion which had already made several collisions. After these collisions it would resemble the positive ion more than the original electron. Accordingly, if the great difference in V' for the negative and positive ions is to be attributed to a difference in their structure, it would be expected that this difference should disappear after a few collisions, and that no ionization by collision of negative ions which had made such previous collisions would occur.

This view is not adopted by Townsend; he assumes that the properties of the negative ion remain unchanged however many collisions it makes. If his assumption is true, the conclusion would seem to follow that the negative ion must remain an electron throughout its history, and not collect round it neutral molecules. The theory will be developed first on this assumption; later it will be considered how the theory is modified if the negative ion changes its properties after a few collisions.

4. The gas is supposed to be contained between parallel electrodes, of which the distance apart, parallel to the axis of x , is l . The difference of potential between the electrodes is V , and the uniform electric intensity between them

* To be published in the April number.

$X = V/l$. Let $N = N_0 p$ be the number of collisions made by an ion in travelling 1 cm. in the direction of x ; p is the pressure of the gas. Then, if q_0 is the number of ions starting from the origin and q the number arriving without previous collision at x , we have, since $N dx$ is the number of collisions made in a layer dx ,

$$-\frac{dq}{dx} = qN, \quad (1)$$

$$\text{or} \quad q = q_0 e^{-Nx}. \quad (2)$$

Let b be the smallest distance through which the ions must fall freely in order to be able to ionize at the next collision, so that

$$b = \frac{V'l}{V} = \frac{V'}{X}. \quad (3)$$

Then e^{-Nb} is the chance that an ion starting from a given layer will travel a distance b parallel to x without making a collision, and $N e^{-Nb} dx$ is the chance that, after travelling freely for that distance, it will make a collision in a layer of thickness dx . Following Townsend, we shall write

$$\alpha = \alpha_0 p = N e^{-Nb}. \quad (4)$$

5. Townsend now proceeds to argue as follows:—Let n_1 be the number of negative ions liberated per second at the surface of the positive electrode, $n_0 p dx$ the number liberated per second by the external ionizing agent (rays of various descriptions) in any layer of the gas of thickness dx at a pressure p . Let $f(x)$ be the number of ions entering from the positive side a layer of thickness dx at a distance x from the positive electrode per second. Then $f'(x) dx$ is the number of ions liberated per second in that layer. These ions are due to two agencies: first, the external ionizing agent, giving a number $n_0 p dx$; second, the collisions of ions liberated in previous layers which have travelled a distance not less than b before arriving at the layer. The number of these collisions Townsend makes equal to the number of ions passing through the layer per second multiplied by the chance that an ion travels a distance not less than b and then makes a collision. He thus obtains

$$f'(x) = n_0 p + \alpha f(x). \quad (5)$$

Or, since $f(x) = n_1$, when $x = 0$,

$$f(x) = \left(n_1 + \frac{n_0}{\alpha_0} \right) e^{\alpha x} - \frac{n_0}{\alpha_0}. \quad (6)$$

The number arriving at the negative electrode is $f(l)$; so that, if i is the current received by that electrode and e the charge on an ion,

$$i/e = \left(n_1 + \frac{n_0}{\alpha_0} \right) e^{\alpha_0 l} - \frac{n_0}{\alpha_0}. \quad . \quad . \quad . \quad (7)$$

6. It is immediately clear that this formula cannot be completely accurate; for, if V is less than V' , there can be no ionization by collision according to the theory, and consequently $f(l)$ for all values of V less than V' should be constant and equal to $n_1 + n_0 p l$; this condition is not fulfilled by (7). A little consideration discloses the source of the error. Townsend assumes that the proportion of the ions passing through any given layer which have travelled freely a distance sufficient to enable them to ionize at their next collision is constant and independent of the position of the layer. This assumption cannot be true, for, if the layer is distant less than b from the positive electrode, none of the ions in that layer can possibly have travelled a distance b ; the frac ion is here zero, while elsewhere it is finite.

In order to estimate rightly the number of ions passing per second through the layer x which, having travelled freely a distance not less than b , will make collisions and produce fresh ions in that layer, we must consider, not the total number of ions passing through the layer x , but the total number passing through the layer $(x-b)$. As will be seen from § 4, αdx is not the chance that an ion in the layer x has travelled a distance b freely and makes a collision in that layer, but the chance that an ion in the layer x will travel a distance b freely and make a collision in the layer $(x+b)$; these two chances are not identical. The ions passing through any given layer are not a random collection in respect of the distance that they have travelled previously to arriving at that layer; for some of them are known to have been produced in the layer; but the ions in any given layer are a random collection in respect of the distance that they will travel after leaving the layer, for this distance is independent of the distance that they have travelled previously.

7. Accordingly, the number of ions passing per second through the layer x which produce fresh ions by collisions in it is the number passing through the layer $(x-b)$ per second multiplied by the chance that an ion in that layer travels a distance b and then makes a collision. In place of (5) we get

$$f'(x) = n_0 p + \alpha f(x-b). \quad . \quad . \quad . \quad (8)$$

8. This equation is an accurate expression of the theory, but, in order to solve it, it is necessary to depart from the theory. For if n_1 is finite, neither $f(x)$ or $f'(x)$ is continuous; both functions obviously have a discontinuity at $x=0$, and the form of (8) shows that they will also have a discontinuity at $x=mb$, where m is any integer. If $n_1=0$, but n' is finite, $f'(x)$, but not $f(x)$, will be discontinuous at $x=0$, but both functions will again be discontinuous at all values of m other than 0. Now it is possible to calculate accurately according to the theory what should be the current between electrodes a distance l apart in a gas at pressure p , when X has a given value, but the calculations are extremely complex, and the resulting formula for the relation between i, l, p, X is not of a form to which Townsend's measurements can be applied. We will therefore assume that $f(x)$ and $f'(x)$ are continuous, and examine the results we obtain.

If $f(x)$ is continuous it must have, in order to satisfy (8), the form

$$f(x) = A e^{\beta x} - \frac{n_0}{\alpha_0}, \dots \dots \dots (9)$$

$$\text{where} \quad \beta = \alpha e^{-\beta b} \dots \dots \dots (10)$$

To determine A use must be made of a known value of $f(x)$ for some value of x . Now between $x=0$ and $x=b$, $f(x)$ must have the form

$$f(x) = n_1 + n_0 p x \dots \dots \dots (11)$$

It is clear that no value of A will give this form to $f(x)$ for all values of x within the range, and a choice must be made. If we choose $x=0$ we get

$$A = n_1 + \frac{n_0}{\alpha_0}, \dots \dots \dots (12)$$

if we choose $x=b$ we get

$$A = \left\{ n_1 + n_0 \left(p b + \frac{1}{\alpha_0} \right) \right\} e^{-\beta b} \dots \dots \dots (12')$$

Now, since we are concerned experimentally with the value of $f(x)$ for $x=l$, where l is greater than b , we are likely to get the more accurate results if we fit the curve to the larger value of x . Accordingly, taking (12') we get

$$i/e = f(l) = e^{\beta l} \left\{ n_1 + n_0 \left(p b + \frac{1}{\alpha_0} \right) \right\} e^{-\beta b} - \frac{n_0}{\alpha_0} \dots \dots (13)$$

It is advisable to transform (13) slightly in order to apply it

to Townsend's measurements, where the values of X/p and not of X are given. Writing $X/p = z$, $\beta = \beta_0 p$ we have

$$pb = \frac{V'}{z} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$\beta_0 = \alpha_0 e^{-\beta_0 \frac{V'}{z}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$\alpha_0 = N_0 e^{-N_0 \frac{V'}{z}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$i/\epsilon = e^{\beta_0 pl} \left\{ n_1 + n_0 \left(\frac{V'}{z} + \frac{1}{\alpha_0} \right) \right\} e^{-\beta_0 \frac{V'}{z}} - \frac{n_0}{\alpha_0} \quad . \quad (13')$$

It was noted that Townsend's formulæ were unsatisfactory because they did not lead to the right value of $f(l)$ when $V = V'$. The formula (13') obviously leads to the right value, for it has been fitted to $x = b$, and when $V = V'$ $l = b$. It also leads to the right value, $f(l) = n_1$ for all values of V when $p = 0$.

9. The only experiments by Townsend which are sufficiently detailed and accurate to enable a comparison to be made between equations (5) and (13') are those on ionization by ultra-violet light. In these conditions $n_0 = 0$, and both equations reduce to the simple exponential form

$$i/\epsilon = P e^{Ql} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where, according to (5), $P = n_1$, $Q = \alpha$, and according to (13') $P = n_1 e^{-\beta b}$, $Q = \beta$.

n_1 is the value of i/ϵ when either $p = 0$ or V is less than V' ; but, since Townsend does not give the values of this quantity in his experiments, it is impossible to use it to test the two formulæ by a comparison of the observed and calculated values of P . The test must be made by means of Q . Townsend deduces from his equations the value of Q/p for a number of values of z , and then uses (4) to calculate values for N_0 and V' ; the concordance between the observed values of Q/p and the values of α_0 deduced from N_0 and V' is taken as a test of the accuracy of the theory. The same procedure can be adopted if $Q = \beta$; for we have the following equation to determine N_0 and V' from the relation between Q/p and z :—

$$\log \beta_0 + \beta_0 \frac{V'}{z} = \log N_0 - N_0 \frac{V'}{z} \quad . \quad . \quad . \quad (18)$$

This calculation has been carried out and the results are given in Tables I.-VIII. Townsend found that the calculated and observed values did not agree for small values

of z , and used only the larger values to determine N_0 and V . The discrepancy is not nearly so marked if Q is taken as equal to β and not to α , but the same procedure has been adopted; only values of Q/p to the left of the asterisk have been used in computing the values of N_0 and V' .

At the head of each table are given the values of N_0 and V' deduced respectively on the assumption that $Q=\alpha$ and that $Q=\beta$. The first row of the table gives the value of z ; the second those of Q/p , the exponential coefficient given by the observations; the third and fourth rows give the differences between this observed value and the values of α_0 and β_0 respectively calculated from the appropriate values of N_0 and V' .

It may be noted that the comparison effected in the last two rows is rather more favourable to equation (5) than to (13'), for the greater complexity of the latter has made it necessary to adjust to a minimum the sum of the squares of the residuals of (18), and not $\Sigma(Q/p-\beta_0)^2$, whereas Townsend's figures are adjusted so that $\Sigma(Q/p-\alpha_0)^2$ is a minimum.

TABLE I.

Air.

$$(Q=\alpha) \quad N_0=14.6, \quad V'=25.0.$$

$$(Q=\beta) \quad N_0=17.93, \quad V'=19.00.$$

| z | 1000 | 800 | 700 | 600 | 500 | 400 | 300 | * | 200 | 100 |
|------------------------|-------|-------|-------|-------|-------|-------|-------|---|-------|-------|
| Q/p | 10.5 | 9.3 | 8.7 | 7.9 | 7.0 | 5.82 | 4.4 | | 2.6 | 0.72 |
| $Q/p-\alpha$ calc. ... | +0.4 | 0.0 | +0.1 | 0.0 | 0.0 | 0.03 | +0.1 | | +0.26 | +0.34 |
| $Q-\beta$ calc. | +0.04 | -0.08 | +0.01 | -0.01 | -0.07 | +0.02 | +0.03 | | +0.04 | +0.18 |

TABLE II.

Nitrogen.

$$(Q=\alpha) \quad N_0=12.4, \quad V'=27.6.$$

$$(Q=\beta) \quad N_0=16.70, \quad V'=21.30.$$

| z | 600 | 500 | 400 | 300 | 200 | 100 | * |
|------------------------|-------|-------|------|-------|-------|-------|---|
| Q/p | 7.0 | 6.2 | 5.2 | 3.95 | 2.3 | .42 | |
| $Q/p-\alpha$ calc. ... | 0.0 | -0.25 | -0.1 | 0.0 | +0.06 | +0.01 | |
| $Q/p-\beta$ calc. ... | -0.16 | -0.08 | 0.0 | +0.07 | +0.06 | -0.15 | |

TABLE III.

Hydrogen.

$$\begin{aligned} (Q=\alpha) \quad N_0 &= 5.0, & V' &= 26.0. \\ (Q=\beta) \quad N_0 &= 6.46, & V' &= 20.4. \end{aligned}$$

| z | 400 | 300 | 200 | 100 | 50 | * | 30 |
|------------------------|-------|-------|-------|-------|------|---|-------|
| Q/p | 3.7 | 3.3 | 2.62 | 1.36 | .36 | | .08 |
| $Q/p-\alpha$ calc. ... | +0.06 | +0.06 | 0.00 | +0.01 | -.01 | | +0.04 |
| $Q/p-\beta$ calc. ... | -0.16 | -0.04 | +0.05 | +0.05 | -.04 | | +0.03 |

TABLE IV.

Carbon Dioxide.

$$\begin{aligned} (Q=\alpha) \quad N_0 &= 20, & V' &= 23.3. \\ (Q=\beta) \quad N_0 &= 22.7, & V' &= 17.0. \end{aligned}$$

| z | 1200 | 1000 | 800 | 700 | 600 | 500 | 400 | * | 300 | 200 | 100 |
|------------------------|-------|-------|-------|-------|-------|------|------|---|-------|-------|-------|
| Q/p | 13.7 | 12.6 | 11.0 | 10.2 | 9.1 | 7.8 | 6.4 | | 4.8 | 2.8 | 0.82 |
| $Q/p-\alpha$ calc. ... | +0.1 | +0.1 | -0.2 | -0.1 | -0.1 | -0.1 | +0.2 | | +0.56 | +0.8 | +0.62 |
| $Q/p-\beta$ calc. ... | -0.16 | -0.14 | +0.09 | +0.01 | +0.08 | -0.2 | +0.1 | | +0.01 | +0.17 | +0.20 |

TABLE V.

Hydrochloric Acid.

$$\begin{aligned} (Q=\alpha) \quad N_0 &= 22.2, & V' &= 16.5. \\ (Q=\beta) \quad N_0 &= 25.03, & V' &= 12.14. \end{aligned}$$

| z | 1500 | 1000 | 800 | 700 | 600 | 500 | 400 | * | 300 | 200 | 100 |
|------------------------|-------|-------|-------|-------|-------|-------|-------|---|-------|------|-------|
| Q/p | 17.5 | 15.4 | 14.0 | 13.0 | 11.9 | 10.5 | 8.9 | | 6.8 | 4.1 | 1.21 |
| $Q/p-\alpha$ calc. ... | 0.0 | 0.0 | 0.0 | -0.2 | -0.1 | -0.15 | -0.0 | | +0.3 | +0.6 | +0.64 |
| $Q/p-\beta$ calc. ... | -0.12 | +0.05 | +0.15 | +0.04 | +0.04 | -0.05 | -0.02 | | -0.07 | -0.0 | |

TABLE VI.

Water Vapour.

$$\begin{aligned} (Q=\alpha) \quad N_0 &= 12.9, & V' &= 22.4. \\ (Q=\beta) \quad N_0 &= 14.12, & V' &= 15.80. \end{aligned}$$

| z | 1000 | 900 | 800 | 700 | 600 | 500 | 400 | * | 300 | 200 | 100 |
|------------------------|-------|-------|-------|-------|-------|------|-------|---|-------|-------|-------|
| Q/p | 9.7 | 9.4 | 9.0 | 8.5 | 7.95 | 7.2 | 6.35 | | 5.2 | 3.6 | 1.31 |
| $Q/p-\alpha$ calc. ... | 0.0 | +0.05 | +0.1 | -0.04 | -0.01 | 0.0 | +0.10 | | +0.3 | +0.6 | +0.60 |
| $Q/p-\beta$ calc. ... | +0.01 | +0.06 | +0.05 | +0.03 | -0.04 | 0.00 | +0.04 | | +0.08 | +0.09 | +0.06 |

TABLE VII.

Argon.

$$(Q=\alpha) \quad N_0=13.6, \quad V'=17.3.$$

$$(Q=\beta) \quad N_0=15.54, \quad V'=12.62.$$

| | | | | | | | | |
|------------------------|-------|-------|------|-------|------|---|-------|-------|
| z | 600 | 500 | 400 | 300 | 200 | * | 100 | 50 |
| Q/p | 9.2 | 8.5 | 7.5 | 6.2 | 4.4 | | 2.0 | 0.58 |
| $Q/p-\alpha$ calc. ... | 0.0 | 0.0 | 0.0 | 0.0 | +0.2 | | +0.7 | 0.46 |
| $Q/p-\beta$ calc. ... | -0.03 | -0.09 | 0.00 | -0.02 | 0.00 | | +0.24 | +0.23 |

TABLE VIII.

Helium.

$$(Q=\alpha) \quad N_0=2.4, \quad V'=14.5.$$

$$(Q=\beta) \quad N_0=3.45, \quad V'=11.02.$$

| | | | | | | | |
|------------------------|-------|-------|-------|-------|-------|---|--------|
| z | 60 | 50 | 40 | 30 | 20 | * | 10 |
| Q/p | 1.35 | 1.20 | 1.00 | 0.77 | 0.40 | | 0.12 |
| $Q/p-\alpha$ calc. ... | +0.01 | 0.00 | -0.01 | +0.02 | -0.02 | | +0.046 |
| $Q/p-\beta$ calc. ... | -0.03 | -0.02 | 0.00 | +0.03 | +0.01 | | -0.03 |

10. It will be observed that, except in the cases of nitrogen and hydrogen, for which Townsend's figures agree peculiarly well with his theory, the assumption that $Q=\beta$ gives a better agreement between the observed and calculated numbers than the assumption that $Q=\alpha$; the difference is especially well marked for smaller values of z . Even in the case of the former assumption there is some systematic divergence in this region; a brief examination of the results which would be obtained, if it were not assumed that $f(x)$ is continuous, but the calculations carried through by examining in detail the history of the ions produced in each layer of the gas, shows that a divergence of the nature found might be caused by the error in this assumption. On the other hand, it is noticeable that the divergence is greater for gases which contain atoms of different kinds, a case which the theory has not attempted to consider. On the whole, it will be concluded universally that the tables afford no reason whatever for believing that the main physical assumptions on which the theory is based are not completely accurate. The correction of the slip in the mathematical work increases the confidence in the foundations of the theory.

The newly calculated values of V' are consistently lower, and the newly calculated value of N_0 consistently higher, than

those given by Townsend. On p. 30 of his book Townsend points out that the value of N_0 leads to an estimate of the radius of a molecule of the gas concerned and finds that the radii calculated by this method are somewhat smaller than those deduced by the ordinary methods of the dynamical theory of gases, based on observations of viscosity, &c. The increase in the value of N_0 due to the revised calculations leads to a nearer approximation between the values of the radius calculated by the two methods, but the correction is not sufficiently large to abolish the difference. It has been pointed out in § 3 that the error introduced by assumption (2) tends to make the values of N_0 , and therefore of the radius of the molecule, too small.

11. It will now be of interest to consider the other of the two alternative hypotheses mentioned in § 3, concerning the nature of the negative ion, and to discover in what way the theory will be altered by adopting it.

It is now supposed that the electron, which represents the negative ion immediately after its formation, can collect round it neutral molecules at subsequent collisions, and thus lose its power of ionizing by collision, except when the electric field is very much greater than that considered in the experiments under discussion. The simplest hypothesis which can be made in this direction, and that which seems on general grounds most likely to be true, is that, when an electron collides with a neutral molecule after travelling freely under the field a distance less than b and fails to ionize it, it adheres to that neutral molecule and forms what we shall call a "complex ion." Accordingly, on this hypothesis, an electron after it has once made a collision at which it fails to ionize the molecule with which it collides can never again ionize on collision in the conditions considered here. However it retains its charge and contributes to the current i in the same way as if it had remained a free electron.

12. Let $f(x)$ be still the number of free electrons entering from the positive side a layer of gas distant x from the positive electrode in one second; let $g(x)$ be the corresponding number of complex ions for the same layer. We shall now have

$$i/\epsilon = f(l) + g(l). \quad . \quad . \quad . \quad . \quad (19)$$

$g'(x)$ is the number of complex ions formed per second in the layer x . On our theory it must also be the number of the free electrons which in that layer collide for the first time with a neutral molecule, having previously travelled

freely a distance less than b . Accordingly all these free electrons have been produced between x and $x-b$. If the number of free electrons produced per second in any layer is q_x , since the probability that an electron produced at $x-y$ collides for the first time at x is $N e^{-Ny}$, where

$$g'(x) = \int_0^b q_{x-y} N e^{-Ny} dy. \quad (20)$$

q_x is not, as before, equal to $f'(x)$, for the value of $f(x)$ as we cross any layer is changed not only by the number of electrons produced there, but also by the number of electrons which disappear there, forming complex ions. In fact,

$$f'(x) = q_x - g'(x). \quad (21)$$

To determine q_x the considerations which lead to (8) are still valid, and we have

$$q_x = n_0 p + \alpha f(x-b). \quad (22)$$

The functions concerned here are, of course, discontinuous in just the same way as those considered previously. In order to proceed further in this direction it is again necessary to assume that they are continuous, and the conditions necessary to determine the integration constants will again be taken as those at $x=b$. If we again take

$$f(x) = A e^{\beta x} + B, \quad (23)$$

we get

$$\beta = \alpha e^{-\beta b} \left\{ 1 - \frac{N}{N + \beta} (1 - e^{-\overline{N + \beta} \cdot b}) \right\}. \quad (24)$$

We shall have four integration constants, A , B , and two derived from integrating (20) to find $g(x)$. To determine these we have the four independent conditions at $x=b$,

$$f(b) = n_1 e^{-Nb} + \int_0^b n_0 p e^{-Ny} dy, \quad (25)$$

$$g(b) = n_1 + n_0 p b - f(b), \quad (26)$$

$$g'(b) = n_1 N e^{-Nb} + \int_0^b n_0 p N e^{-Ny} dy, \quad (27)$$

$$q_b = n_0 p + \alpha n_1.$$

The resulting equations are so complicated that no attempt has been made to apply them to experiments. But it may be noted that, in place of the simple exponential form (17) when $\nu_0=0$, we obtain

$$i/\epsilon = Pe^{\beta b} + Ql + R. \quad . \quad . \quad . \quad . \quad (17')$$

Accordingly, if this theory were correct, the curves obtained by Townsend should not have been accurately exponential. Sufficient measurements are not given to test this point, but the fact that consistent values of the exponential coefficient were obtained from different pairs of points, on the assumption that the curve was exponential, is some evidence against the second theory. But the distinction between the two theories can be best made by examining the calculated and observed relations between n_1 and n' and those constants in the equations which involve them. Townsend gives no values for n_1 , and hence this test cannot be applied. The experiments described in the next paper appear to provide a conclusive proof in favour of the first theory and against the second.

Summary.

1-3. The physical assumptions made in Townsend's theory of ionization by collision are analysed and discussed. It is pointed out that one of them is to the effect that the negative ion does not undergo any permanent change in its properties as a consequence of repeated collisions with neutral molecules. This assumption is contradictory to the older view of ionization by collision, according to which the negative ion, when first formed, is an electron, but subsequently becomes a "complex ion" by gathering round it neutral molecules.

4, 5. Townsend's mathematical argument, by which he applies these assumptions to certain cases of the discharge through gases, is sketched briefly.

6-8. It is pointed out that this argument contains an error. No attempt is made to arrive at completely accurate formulæ, but a nearer approximation is made.

8, 9. The new formulæ are applied to Townsend's measurements, and shown to agree with them better than those which he used.

10-12. Similar formulæ are briefly sketched based on the older view that a negative ion after collisions with neutral molecules becomes a complex ion. Townsend's experiments are not so well suited for distinguishing between the two

theories as those described in the following paper *. Further discussion of this point is, therefore, postponed until the account of that work is complete.

Leeds University,
Nov. 18, 1911.

Note added Feb. 10.

Mr. Bishop has recently (*Phys. Zeits.* xii. p. 1148, 1911) published an account of a very complete experimental test of the accuracy of Townsend's theory. His formula differs slightly from that of Townsend in the nature of the relation between α and the quantities N and V' , but it appears to me open to the same criticism as has been made in this paper, in that it does not reduce to the right form when l is less than b . The absence of a divergence between observed and calculated values is probably due to the fact that throughout his experiments l was much greater than b .

XXXVII. *Concerning the Thermal Expansion of Mercury, Remarks on a Paper by Callendar and Moss.* By KARL SCHEEL and WILHELM HEUSE †.

1. **A**BOUT a year ago Callendar and Moss ‡ published the results of a comprehensive investigation of the thermal expansion of mercury, in which they used the method of balanced hydrostatic tubes. The authors themselves state that there is a considerable difference between their results and those obtained by Chappuis § in the Bureau international des Poids et Mesures. They raise the objection against the measurements of Chappuis, who used the dilatometer method, that it is not allowable to calculate the cubical expansion of a body by multiplying its linear expansion measured in only one direction by 3, since the hereby assumed isotropy of the body is not certain.

One might consider perhaps that this objection is correct, if, as Callendar and Moss have done, only the results of Chappuis for the expansion of mercury are discussed. In reality, however, a proper opinion concerning the reliability

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† Communicated by the Authors from the Physikalisch-Technischen Reichsanstalt.

‡ Hugh L. Callendar and Herbert Moss, *Phil. Trans. (A)* 211. pp. 1-32 (1911).

§ P. Chappuis, *Trav. et Mém. du Bureau international des Poids et Mesures*, xiii. C, 31 pp., 1903 (1907).