THE THEORY OF IONIZATION BY COLLISION.

I. The Distribution of Velocities of the Electrons.

By K. T. Compton.

Introduction.—The fundamental equation in any theory of ionization of gases by impact is

$$n = n_0 \frac{(\alpha - \beta)\epsilon^{(\alpha-\beta)d}}{\alpha - \beta\epsilon^{(\alpha-\beta)d}}, \qquad (1)$$

where n_0 is the number of negative ions which start per second from the negative electrode, n is the number per second which reach the positive electrode and α and β are the average numbers of new ions of either sign formed per centimeter path by each negative and positive ion respectively. In many cases the ionization is due almost entirely to the negative ions and equation (1) reduces to

$$n = n_0\epsilon^{\alpha d}. \qquad (2)$$

These equations were first proposed by Townsend[1] and are correct on any theory of ionization due exclusively to collisions. They afford no information concerning the mechanism by which impacts may result in the formation of new ions.

Attempts to derive, from assumptions regarding the nature of ionization, expressions for α and β in terms of properties of the colliding particles have not been very successful. Townsend[2] assumed that collisions of electrons with molecules are inelastic, that ionization occurs at an impact if the velocity of the electron exceeds a critical value characteristic of the gas and that no appreciable recombination or formation of "clusters" occurs within the range of electric fields and pressures used in the experimental tests. The resulting formula for α agreed so well with the facts then known that these assumptions have been rather generally accepted as at least approximately true. However we know now that the constants in Townsend's formula differ from the correct values in most cases by more than a hundred per cent., being in some cases too large and in others too small. Moreover the equation is not successful for small fields and in the case of helium (and probably the other inert gases) the plotted curves are not even of the right general shape.

[1] "Ionization of Gases by Collision," pp. 4, 41.

[2] Ibid., p. 23.

Campbell[1] recently pointed out an error in the derivation of Townsend's formula. The corrected equation conforms slightly better to the experimental results, but the difference is not great and the constants are still far from correct.

The most satisfactory equation for α which has been proposed was derived by Bergen Davis[1] on assumptions similar to Townsend's except that the necessary condition for ionization at an impact is that the colliding electron must possess a velocity whose component normal to the surface of the molecule (considered spherical) exceeds a critical velocity characteristic of the gas. For many gases this formula fits the facts acceptably over a wide range of pressures and gives much more accurate values of the constants than does Townsend's formula. But it also fails in the case of helium and the other inert gases. Moreover it will be shown that certain conditions exist in the ionized gas which necessitate a modification of Bergen Davis's formula.

It appeared to the writer that a study of the distribution of velocities of the ions in the gas under various conditions should be of value in forming a theory of ionization by collision. The present paper gives the more important results of a study of the velocity distribution. On this foundation expressions for α have been derived which conform more nearly to the facts than any formula yet suggested and which may be applied to the inert gases and to mixtures of gases. The derivation and discussion of these equations will be given in a later paper.

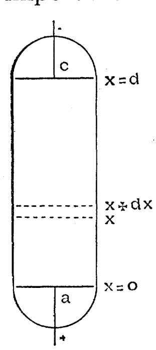

Fig. 1.

Notation.—For convenient reference the uniform notation employed is explained here. Let c be the cathode and a the anode in a discharge tube. By ultra-violet light, or otherwise, electrons are liberated from c and move toward a under the influence of the applied field. We shall let

x = distance from anode a measured in the direction of the potential drop;
d = distance between anode a and cathode c;
X = electric intensity (supposed uniform);
n_0 = number of electrons leaving c per second;
n = number of electrons passing plane x per second;
n_a = number of electrons reaching a per second;
ν = average number of collisions made by an electron in traveling one centimeter in the direction of the electric force;

[1] Phil. Mag., 23, p. 400 (1912).
[2] PHYS. REV., 24, p. 93 (1907).

P = probability that an electron ionizes when it collides;
P_x = probability that an electron goes a distance x without being stopped by a collision;
α = number of ionizing collisions by an electron per centimeter path;
β = number of ionizing collisions by a positive ion per centimeter path;
p = pressure of the gas;
e, m = charge and mass of an electron;
$F(v)dv$ = probability that an electron has a velocity between v and $v + dv$;
$F(x)dx$ = probability that it has moved freely a distance between x and $x + dx$;
$F(V)dV$ = probability that it has a velocity due to a potential drop between V and $V + dV$;
n', ν', P', P_x' are the corresponding quantities which refer to the positive ions.

It has been recently shown,[1] as was previously suspected, that in some gases the electrons start approximately from rest after each collision while in others their kinetic energy is retained except at collisions which result in ionization. We shall call these cases of inelastic and elastic impact, respectively, and shall consider first the case of ionization by electrons only, which occurs when X/p and d are small. We shall be safe in assuming that no appreciable recombination or formation of "clusters" occurs within the range of pressures and electric fields employed in measurements of ionization by collision.[2]

A. Inelastic Impact.

(1) *Ionization Due Exclusively to Electrons.*

Consider the electrons colliding and originating in a layer dx distant x from the anode a (Fig. 1). The number of collisions per second in this layer is $n\nu dx$. Of these collisions, $Pn\nu dx$ result in the formation of new ions. Thus $(1 + P)n\nu dx$ ions start from rest in the layer dx each second. According to the kinetic theory of gases the probability that one of these will reach the anode a without further collisions is

$$P_x = \epsilon^{-\nu x}. \tag{3}$$

Thus

$$n_a F(x)dx = (1 + P)n\nu\epsilon^{-\nu x}dx$$

[1] Franck and Hertz, Verh. d. D. Phys. Ges., 15, p. 373 (1913); 16, p. 457 (1914).
[2] Townsend, Phil. Mag., 23, p. 856 (1912).

is the number of electrons reaching a per second after having traveled freely a distance between x and $x + dx$.

But in the layer dx the total number of electrons has been increased by the number $dn = -P n \nu dx$, whence

$$n = n_a \epsilon^{-P\nu x}. \tag{4}$$

Substituting this value of n we obtain

$$F(x)dx = (1 + P)\nu \epsilon^{-(1+P)\nu x} dx. \tag{5}$$

These reach a with a velocity determined by the relations

$$\tfrac{1}{2}mv^2 = eV = eXx; \tag{6}$$

whence

$$F(V)dV = (1 + P)\frac{\nu}{X}\epsilon^{-(1+P)\frac{\nu V}{X}} dV, \tag{7}$$

and

$$F(v)dv = (1 + P)\frac{\nu m v}{eX}\epsilon^{-(1+P)\frac{\nu m v^2}{2eX}} dv. \tag{8}$$

Now it is a well-known theorem in the kinetic theory of gases that the molecules which pass a plane in a gas have components of velocity normal to the plane whose distribution is given by an equation of the form

$$F(u)du = Au\epsilon^{-Bu^2} du.$$

By comparison with equation (8) it is seen that the electrons in the discharge tube reach the anode a with velocities distributed according to Maxwell's law. The average velocity with which they arrive is

$$v = \int_0^\infty vF(v)dv = \sqrt{\frac{\pi e X}{2(1 + P)\nu m}}$$

and the most probable velocity is

$$v = \sqrt{\frac{eX}{(1 + P)\nu m}}. \tag{9}$$

We have assumed here that the discharge tube is of infinite length. If it is of length d the initial velocity distribution $f(v)dv$ at c must be considered and the probability of ionization at a collision cannot be considered independent of x. Under these conditions an argument similar to that used to derive equation (8) leads to

$$\begin{aligned} F(v)dv = {} & \left[\epsilon^{-\nu\left(d + \int_0^d P dx\right)} f(v - v') \right]_{v=v'}^{v=\infty} \\ & + \left[(1 + P)\frac{\nu m v}{eX}\epsilon^{-\frac{\nu m}{eX}\left(\frac{v^2}{2} + \int_0^v P v dv\right)} dv \right]_{v=0}^{v=v'}, \end{aligned} \tag{10}$$

where v' is the velocity gained in a free passage from c to a. This expression reduces to equation (8) when d and v' are infinite and P is constant. The first term arises from those electrons which pass from c to a without suffering a collision and gives a velocity distribution identical with that of the emitted electrons increased by the amount v'. The second term gives the velocity distribution of those which have undergone collision or been produced in the gas and applies only to velocities less than v'. There is thus a discontinuity in the function $F(v)$ at $v = v'$.

Fortunately equation (10) becomes practically identical with (8) when d exceeds several mean free paths l. I have therefore used equation (8), or its equivalent (7), as the basis of part of the theory of ionization and in applying experimental results as a test I have rejected the few data taken under conditions in which equation (10) differs appreciably from (8). In the remainder of this paper we shall consider only cases in which d is at least several times greater than l.

(2) *Ionization Due Both to Electrons and to Positive Ions.*

In this case we have, as before, $(1 + P)n\nu dx$ electrons starting from rest in the layer dx every second as the result of collisions by electrons in this layer. In addition $P'n'\nu'dx$ electrons are formed per second by the impacts of positive ions. Thus $[(1 + P)n\nu + P'n'\nu']dx$ electrons start from rest in dx each second. Therefore

$$n_a F(x)dx = [(1 + P)n\nu + P'n'\nu']e^{-\nu x}dx \tag{11}$$

electrons arrive at a from dx each second.

But

$$dn = -[Pn\nu + P'n'\nu']dx = -[Pn\nu + P'(n_a - n)\nu']dx,$$

since of necessity $n_a = n + n'$ at any point in the gas. Integrating this equation we find

$$n = \frac{n_a}{(P\nu - P'\nu')}[P\nu\epsilon^{-(P\nu - P'\nu')x} - P'\nu'],$$

from which

$$n' = \frac{n_a}{(P\nu - P'\nu')}[P\nu - P\nu\epsilon^{-(P\nu - P'\nu')x}].$$

Substituting these values of n and n' in equation (11) and regrouping the terms we find that

$$F(x)dx = \frac{1}{(P\nu - P'\nu')}\{[(1 + P)P\nu^2 - P\nu P'\nu']\epsilon^{-[(1+P)\nu - P'\nu']x} - P'\nu'\nu\epsilon^{-\nu x}\}dx. \tag{12}$$

This equation of course reduces to (5) when $P' = O$ or $\nu' = O$.

By substituting for x from equation (6) we find that the distribution of velocities is given by

$$F(v)dv = \frac{(1+P)P\nu^2 - P\nu P'\nu'}{P\nu - P'\nu'}\frac{mv}{eX}\epsilon^{-[(1+P)\nu - P'\nu']\frac{mv^2}{2eX}}dv - \frac{P'\nu'\nu}{P\nu - P'\nu'}\frac{mv}{eX}\epsilon^{-\nu\frac{mv^2}{2eX}}dv, \quad (13)$$

which is the difference between two Maxwell's distributions and is not itself a Maxwell's distribution except in particular cases. The maximum value of the first term obtains when

$$v = \sqrt{\frac{eX}{m[(1+P)\nu - P'\nu']}} \quad (14)$$

and of the second term when

$$v = \sqrt{\frac{eX}{m\nu}}. \quad (15)$$

When there is no ionization by collision the second term in (13) vanishes and the first comes to a maximum given by equation (15). In case ionization is due entirely to electrons $P'\nu' = O$ and equation (13) reduces to equation (8) with the maximum given by equation (9). The most probable velocity is seen to be less than it would be if there were no ionization. This is due to the fact that those ions formed very near the plate a reach it with velocities below the average. Another particular case of interest occurs when $P\nu = P'\nu'$, or when the positive and negative ions are equally efficient in the production of new ions. Then both terms of (13) combine to give a Maxwell's distribution identical with that found when there is no ionization. In this case the number n of electrons passing a plane in the gas in one second is the same for all positions of the plane. Only when the distance d is very small can this case be realized experimentally; otherwise an arc is set up.

B. Elastic Impact.[1]

Ionization Due Exclusively to Electrons.

The only points in which the treatment of this case differs from that in the case of inelastic impact are in the expressions for the number of electrons starting from rest in any layer and for the probability of reaching a without being stopped. We thus have $2Pn\nu dx$ electrons starting from rest in the layer dx each second and

[1] This treatment is only approximate, since it does not follow the new-formed electrons in their subsequent history. An exact treatment is given in the following paper.

$$Px = \epsilon^{-P\nu x}.$$

Also

$$dn = -Pn\nu dx,$$

whence

$$n = n_a\epsilon^{-P\nu x}.$$

Therefore

$$F(x)dx = 2P\nu\epsilon^{-2P\nu x}dx. \qquad (16)$$

From equations (6)

$$F(V)dV = 2P\frac{\nu}{X}\epsilon^{-2P\frac{\nu V}{X}}dV \qquad (17)$$

and

$$F(v)dv = 2P\nu\frac{mv}{eX}\epsilon^{-2P\nu\frac{mv^2}{2eX}}dv. \qquad (18)$$

The velocity distribution again conforms to Maxwell's law and the most probable velocity is

$$v = \sqrt{\frac{eX}{2P\nu m}}. \qquad (19)$$

By comparison with equation (9) it is seen that the velocities are greater in the case of elastic than in the case of inelastic impact. It will be shown that this accounts quantitatively as well as qualitatively for the relatively large ionization in helium, argon, etc.

A certain amount of caution must be exercised in interpreting ν in these equations. ν refers always to the average number of collisions in one centimeter path in the direction of the electric force. In inelastic impact there is no motion in any other direction except the negligible amount due to the effects of thermal agitation. In the case of elastic impact, however, there is in general a considerable component of velocity perpendicular to the electric force, due to the rebound at elastic collisions. Thus the ν which appears in the formulæ for elastic impact is larger than the reciprocal of the mean free path. Direct measurements of ν in various gases are being made in this laboratory.

C. Ionization in a Mixture of Elastic and Inelastic Gases.

Let P_ϵ and P_i be the probabilities of ionization at an impact of an electron with molecules of the elastic and inelastic gases respectively, and let ν_ϵ and ν_i be the average numbers of collisions with molecules of these gases in one centimeter path of an electron. The relative magnitudes of ν_ϵ and ν_i will vary according to the proportions in which the gases are mixed.

Following the same reasoning as before we find that $n[(1+P_i)\nu_i + 2P_\epsilon\nu_\epsilon]dx$ electrons start from rest in the layer dx each second. $\epsilon^{-\nu_i x}$

is the probability of reaching a without an inelastic collision and $\epsilon^{-P_\epsilon \nu_\epsilon x}$ is the probability of arriving without having been stopped by an ionizing elastic collision. Thus

$$P_x = \epsilon^{-(\nu_i + P_\epsilon \nu_\epsilon)x}.$$

Also

$$dn = -(P_i \nu_i + P_\epsilon \nu_\epsilon) n dx,$$

whence

$$n = n_a \epsilon^{-(P_i \nu_i + P_\epsilon \nu_\epsilon)x}.$$

Therefore

$$F(x)dx = [(1 + P_i)\nu_i + 2P_\epsilon \nu_\epsilon]\epsilon^{-[(1+P_i)\nu_i + 2P_\epsilon \nu_\epsilon]x} dx, \qquad (20)$$

$$F(V)dV = \frac{(1 + P_i)\nu_i + 2P_\epsilon \nu_\epsilon}{X} \epsilon^{\frac{-(1+P_i)\nu_i + 2P_\epsilon \nu_\epsilon V}{X}} dV, \qquad (21)$$

$$F(v)dv = [(1 + P_i)\nu_i + 2P_\epsilon \nu_\epsilon] \frac{mv}{eX} e^{-[(1+P_i)\nu_i + 2P_\epsilon \nu_\epsilon]\frac{mv^2}{2eX}} dv. \qquad (22)$$

In this case also the distribution follows Maxwell's law. Equation (22) reduces to equation (8) when $P_\epsilon \nu_\epsilon = O$ and to equation (18) when $\nu_i = O$.

Expressions for $F(v)dv$ similar to equation (13) may easily be obtained to apply to cases of elastic impact by both positive and negative ions. Since there is yet no evidence of elastic impact by positive ions it has not been thought worth while to include a discussion of this possibility.

The importance of equation (21) will be suggested in a following paper in which it will be shown that the expression for α derived from equation (21) explains the extreme electrical sensitiveness of helium and argon to the slightest traces of ordinary gases and that it accounts for the departure from theory of many experimental results.

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