THE THEORY OF IONIZATION BY COLLISION.

III. Case of Elastic Impact.

By K. T. Compton.

Introduction.—In the preceding paper[1] there was derived an equation by which α, the average number of new ions of either sign formed per centimeter path in a gas by each electron, could be accurately calculated from a knowledge of the potential gradient X, the minimum ionizing potential V_0 and the average number of collisions ν made by each electron in a centimeter path in the direction of X. This equation was shown to accord with experimental results more accurately than any equation hitherto proposed. It was based on the assumption of inelastic impact between electrons and gas molecules and therefore does not apply to such gases as helium, argon and neon in which the collisions have been shown to be elastic,[2] *i. e.*, the kinetic energy of the colliding electron is retained except at impacts which result in ionization. The problem of deriving a theoretical relation between X, α and ν applicable to these gases is much more difficult than in the case of inelastic impact and has, so far as I am aware, been attempted only by Franck and Hertz[3] who did not obtain an equation to which experimental data could be applied.

In the present paper I have succeeded in deriving, for cases of elastic impact, an equation based on the same assumptions as those underlying the theory for inelastic gases developed in the preceding papers. This equation seems to receive very satisfactory experimental support.

Functional Relation between α, X and p.—Townsend[4] has shown that a relation of the form

$$\frac{\alpha}{p} = f\left(\frac{X}{p}\right)$$

must hold in all cases of ionization of gases by inelastic impact. His argument does not necessarily apply in case the collisions are elastic. It is necessary, therefore, to see whether the same type of relation is true in the case of elastic impact.

[1] Phys. Rev., this issue.

[2] Franck and Hertz, Verh. d. D. Phys. Ges., 15, p. 373, 1913; 15, p. 613, 1913; 16, p. 457, 1914.

[3] Verh. d. D. Phys. Ges., 16, p. 12, 1914.

[4] Ionization of Gases by Collision, p. 18.

Let ν represent, as formerly, the average number of impacts by each electron while advancing one centimeter in the direction of the electric intensity X. Let ν_1 represent the average number of impacts by each electron in a centimeter path in any direction. ν_1 is the reciprocal of the mean free path of the electron.

In inelastic gases ν equals ν_1, since there is no component of velocity perpendicular to the electric intensity except that arising from thermal agitation, which is negligible in comparison with the velocity due to the electric field. In the elastic gases, however, there is generally a sidewise component; the electron will bound and rebound many times and in all directions. Thus in the present case ν exceeds ν_1 by an amount which we shall now calculate.

During a free path l the electron experiences an acceleration equal to Xe/m in the direction of the electric field. If $\bar{v}$ is the average velocity of an electron just before it ionizes, $\bar{v}/2$ is its average velocity and hence $2l/\bar{v}$ is the mean free time. Therefore

$$s = \frac{1}{2}at^2 = \frac{1}{2}\frac{Xe}{m}\left(\frac{2l}{\bar{v}}\right)^2$$

gives the average distance moved in the direction of the electric field during one free path. The reciprocal of s is ν, whence

$$\nu = \frac{1}{s} = \frac{m\bar{v}^2}{2Xel^2} = \frac{m\bar{v}^2\nu_1^2}{2Xe}.$$

But Xe is the energy acquired by the electron in moving one centimeter in the direction of the field and $\frac{1}{2}m\bar{v}^2$ is the average energy of the electron when it ionizes. The ratio of these quantities evidently equals α, the number of ionizing collisions made per centimeter by each electron. Thus

$$\nu = \frac{\nu_1^2}{\alpha}, \quad \text{or} \quad \alpha = \frac{\nu_1^2}{\nu}. \tag{28}$$

But $\alpha = P\nu$, where P is the probability that an electron ionizes when it collides. Thus

$$P = \left(\frac{\nu_1}{\nu}\right)^2, \quad \text{or} \quad \nu = \frac{\nu_1}{\sqrt{P}}. \tag{29}$$

Since P is always less than unity, ν always exceeds ν_1. In the limit, with so large a field that ionization would occur at every impact, ν_1 would equal ν and P would equal unity, as is otherwise obvious. This shows that no numerical factor has been neglected in equation (29) owing to the use in the above argument of the average velocity rather than the exact velocity distribution.

Now ν_1 is proportional to the pressure p. Also it is obvious that if X varies as p, then ν varies as p. Thus, from equation (28), if X varies as p then α varies as p; whence

$$\frac{\alpha}{p} = \psi\left(\frac{X}{p}\right). \tag{30}$$

We see, therefore, that the type of functional relation between α, X and p is the same for elastic and inelastic gases; the form of the function ψ is of course different in the two cases.

We shall proceed to determine the form of the function ψ for an elastic gas. It will be convenient to deal with ν instead of ν_1. At the end of the argument equation (29) will enable us to replace ν by the more familiar quantity ν_1.

Determination of $\psi(X/p)$.—As in the case of inelastic impact the probability that any electron, chosen at random, ionizes at an impact with a gas molecule is

$$P = \int_0^\infty f(V)F(V)dV, \tag{31}$$

where $f(V)$ is the probability that an electron with a velocity due to a potential drop V ionizes when it collides and $F(V)dV$ is the probability that an electron possesses a velocity due to a potential drop between V and $V + dV$. For the reasons given in the preceding paper we shall take

$$f(V) = 0 \qquad \text{if} \quad V \leqq V_0,$$

$$f(V) = \frac{V - V_0}{V} \quad \text{if} \quad V \geqq V_0. \tag{32}$$

It remains to determine $F(V)dV$. We shall suppose that the mean free path l and the minimum ionizing path x_0 are small in comparison with the distance between the electrodes of the discharge tube, and in testing the equation so derived we shall reject experimental data taken under circumstances in which this restriction can be shown to lead to an appreciable error. Under these conditions we may take P and ν to be uniform throughout the discharge tube.

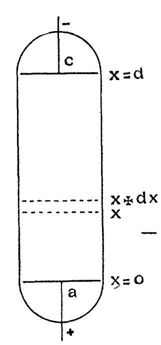

Fig. 3.

Consider the subsequent history of the electrons which start from rest in any layer dx in the gas. (Fig. 3.) Only at an ionizing collision is an electron stopped, whence two electrons start from rest as the result of each ionizing collision in dx. Thus the number of electrons starting from rest in dx per second is $2P\nu n dx$, where n is the number of electrons entering the layer dx per second. The number of new negative ions originating per second in dx is

$$dn = -P\nu n dx,$$

whence

$$n = n_a e^{-P\nu x}. \qquad (33)$$

where n_a is the number per second which reach the anode a. Therefore

$$n_0 = 2P\nu n_a e^{-P\nu x}\, dx \qquad (34)$$

electrons start from rest in dx each second.

If x_0 is the distance which an electron must go in the direction of the electric force in order to acquire the minimum ionizing velocity corresponding to V_0, it is evident that none of the electrons starting in dx can ionize (or be stopped) in going a distance less than x_0. Thus

$$[F(x)dx = 2P\nu e^{-P\nu x}\, dx]_{x=0}^{x=x_0} \qquad (35)$$

applies within the limits noted. In terms of potential drop this is

$$\left[F(V)dV = \frac{2P\nu}{X} e^{-\frac{P\nu}{X}V}\, dV\right]_{V=0}^{V=V_0}. \qquad (35)$$

Equation (35) gives the distribution of velocities of the electrons passing any plane in the gas, for velocities less than the minimum ionizing velocity. For all of these $f(V) = 0$, whence they contribute nothing toward the value of P in equation (31).

Consider now the history of those n_0 electrons after they have gone a distance x_0. We shall call $f(x)$ the probability that one of these ionizes at an impact after having gone a distance x from its starting point in dx. $f(x)$ is obviously identical with $f(V)$ and is equal to $(x - x_0)/x$.

Let n_x be the number of the original n_0 electrons which have not been stopped by ionizations in going the distance x from dx. Of these, $\nu n_x dx'$ will collide in the ensuing layer dx'. Thus $f(x)\nu n_x dx'$ of the original n_0 electrons are stopped by ionization in the layer dx' distant x from dx. In other words

$$dn_x = -f(x)\nu n_x dx',$$

whence

$$n_x = n_0 e^{-\int_{x_0}^{x} f(x)\nu dx'} = n_0 e^{-\nu\int_{x_0}^{x}\frac{x-x_0}{x}dx'}$$

$$= n_0 \left(\frac{x}{x_0}\right)^{\nu x_0} e^{-\nu(x-x_0)}.$$

Thus

$$\frac{n_x}{n_0} = \left(\frac{x}{x_0}\right)^{\nu x_0} e^{-\nu(x-x_0)}$$

is the probability that an electron, originating in dx, goes a distance x, ($x \geqq x_0$), without being stopped.

From this quantity and equation (35) we obtain

$$\left[F(x)dx = 2P\nu\left(\frac{x}{x_0}\right)^{\nu x_0} e^{\nu x_0} e^{-\nu(1+P)x} dx \right]_{x=x_0}^{x=\infty}, \tag{36}$$

or

$$\left[F(V)dV = \frac{2P\nu}{X}\left(\frac{V}{V_0}\right)^{\frac{\nu V_0}{X}} e^{\frac{\nu V_0}{X}} e^{-(1+P)\frac{\nu V}{X}} dV \right]_{V=V_0}^{V=\infty}, \tag{36}$$

for the velocity distribution, in terms of potential drop, of those electrons which are able to ionize while passing through any plane of the gas.

Finally, substituting from equations (32) and (36) in (31) we find

$$P = \int_{V_0}^{\infty} \frac{V - V_0}{V} \frac{2P\nu}{X} e^{\frac{\nu V_0}{X}} \left(\frac{V}{V_0}\right)^{\frac{\nu V_0}{X}} e^{-(1+P)\frac{\nu V}{X}} dV,$$

or, in terms of x,

$$P = \int_{x_0}^{\infty} 2P\nu e^{\nu x_0} \frac{x - x_0}{x} \left(\frac{x}{x_0}\right)^{\nu x_0} e^{-(1+P)\nu x} dx,$$

which is easily reduced to

$$\frac{x_0^{\nu x_0}}{2\nu e^{\nu x_0}} = \int_{x_0}^{\infty} x^{\nu x_0} e^{-(1+P)\nu x} dx - x_0 \int_{x_0}^{\infty} x^{\nu x_0 - 1} e^{-(1+P)\nu x} dx.$$

In order to plot this equation it will suffice to solve it only for integral values of νx_0, in which case the integrals are of the familiar type $\int x^m e^{ax} dx$. The factorial terms arising from the two integrals may be combined in such a way that the above equation reduces to

$$e^{P\nu x_0} = 2\nu x_0 \left\{ \frac{1}{[\nu x_0(1 + P)]^2} + \frac{2(\nu x_0 - 1)}{[\nu x_0(1 + P)]^3} + \frac{3(\nu x_0 - 1)(\nu x_0 - 2)}{[\nu x_0(1 + P)]^4} + \cdots + \frac{(\nu x_0 - 1)(\nu x_0 - 1)!}{[\nu x_0(1 + P)]^{\nu x_0}} + \frac{\nu x_0!}{[\nu x_0(1 + P)]^{\nu x_0 + 1}} \right\} \tag{37}$$

This is the simplest form of the equation expressing the theory of elastic impact.

The calculation of corresponding values of νx_0 and P from this equation was exceedingly laborious. I gave νx_0 various integral values between 0 and 80 and in each case determined by trial the value of P which satisfied the equation. Some of the values so obtained are given in Table V. Since we wish to deal ultimately with the mean free path l, or its reciprocal ν_1, instead of ν, the values from the above calculations have been translated into terms of ν_1 by the use of equation (29). Instead of x_0 its more useful equivalent V_0/X has been written in Table V.

TABLE V.

$\frac{\nu V_0}{X}$	P	$\frac{\nu_1 V_0}{X}$	$\frac{\nu V_0}{X}$	P	$\frac{\nu_1 V_0}{X}$
0	1.000	0.000	10	0.0478	2.186
1	0.249	0.499	15	0.0337	2.756
2	0.161	0.802	20	0.0265	3.256
3	0.1213	1.045	25	0.0222	3.725
4	0.0984	1.255	30	0.0189	4.124
5	0.0831	1.441	40	0.0144	4.793
6	0.0723	1.613	60	0.0101	6.030
8	0.0574	1.917	80	0.0075	6.940

For any given value of $\nu_1 V_0/X$ the corresponding value of P may thus be found, whence

$$\alpha = P\nu = \nu_1 \sqrt{P} \tag{38}$$

by equation (29).

Experimental Verification of Equation (37).—Experiments on exceedingly pure helium by E. W. B. Gill and F. B. Pidduck[1] enable us to test equation (37). I have applied to their data tests similar to those mentioned in the paper on inelastic impact, whence I have rejected all values

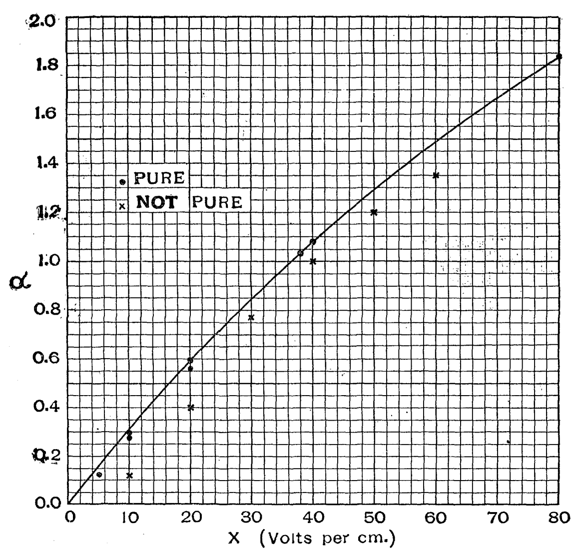

Fig. 4.
Helium.

for which P and ν cannot be considered approximately uniform throughout the ionization chamber. The values have been reduced as suggested by equation (30) to correspond to a pressure of 1 mm. The agreement

[1] Phil. Mag., 23, p. 837, 1912.

between these data and equation (37) is shown by Fig. 4 in which the dots represent the experimental data and the solid curve represents the equations (37) and (38) with the constants V_0 and ν_1 so chosen as to give the best agreement.

Additional support of the theory is found in the calculated values of V_0 and ν_1. In Table VI. the column marked *Exp.* gives the directly determined value of V_0 as published, the column marked *Exp.** gives the revised experimental value which appears to me most probable from a consideration of the experimental results[1] and the fourth column gives the value of V_0 determined by the present theory. Corresponding data from the preceding paper on inelastic impact are included for comparison.

TABLE VI.

Gas.	V_0			ν_1	
	Exp.	Exp.*	Theory.	$\pi R^2 N$	Theory.
He	20.0	22.5	22.5	13.5	10.0
A	12.0	13.5	14.5?	32.0	15.0?
N_2	7.5	10.0	10.05	34.5	22.5
CO_2			8.20	49.5	30.0
H_2O			7.47	47.0	21.7
HCl			6.05	46.0	33.3

Table VI. contains also the values of ν_1 calculated for a pressure of 1 mm. In the fifth column are given values calculated on the assumption that $\nu_1 = \pi R^2 N$, where πR^2 is the molecular cross section calculated from the kinetic theory and N is the number of molecules per unit volume. Where direct test is possible the theoretical values of V_0 appear to be accurate and the values of ν_1 appear to be consistently smaller than $\pi R^2 N$, for which a reason was previously suggested.

In the case of the elastic gas argon the ionization experiments are untrustworthy and the values calculated from them by the present theory can only be regarded as very approximate in view of the following considerations.

Effect of Impurities in the Gas.—Not only is there good agreement between theory and experiment as shown by Fig. 4, but the deviations from the theory are in a direction to be explained by traces of impurities in the gas, as is shown by the crosses which represent experiments in which the helium was known to be less pure.[2] The effect of even slight traces of ordinary gases is to give helium, in small fields, the characteristics of an inelastic gas. In other words, impurities cause the $\alpha - X$ curve

[1] See the preceding paper, *loc. cit.*

[2] E. W. B. Gill and F. B. Pidduck, Phil. Mag., 16, p. 280, 1908.

to leave the origin horizontally instead of at a definite angle. It is not surprising, therefore, that the only available data for argon do not conform accurately to the present theory when we know that the experiments were performed under conditions identical with those in which the crossed data for helium were obtained.[1] The values of V_0 and ν_1 for argon in Table VI. were obtained by constructing a curve which bore the same relation to the data for argon that the curve of Fig. 4 does to the crossed data. These values are, of course, much more uncertain than those for the other gases.

Approximate Theory of Ionization in a Mixture of Elastic and Inelastic Gases.—I have not been able to work out an exact formula to cover this case but will briefly outline a treatment which various tests have shown to be not very far from correct. The equation which we shall derive has its chief value in its ability to account for the effects of small traces of impurities in gases.

Suppose that an electron, in one centimeter path, makes an average of ν_i and ν_e collisions with molecules of inelastic and elastic gases, respectively, and let V_{oi} and V_{oe} be the minimum ionizing potentials in the two gases. By equation (21) in an earlier paper[2] we have, for the velocity distribution among the electrons approximately

$$F(V)dV = \frac{(1 + P_i)\nu_i + 2P_e\nu_e}{X} e^{-\frac{(1+P_i)\nu_i+2P_e\nu_e}{X}V} dV,$$

where P_i and P_e are the probabilities of ionization at an inelastic and an elastic impact, respectively. We have therefore, from equation (31),

$$P_i = \int_{V_{oi}}^{\infty} \frac{V - V_{oi}}{V} F(V)dV = e^{-\frac{sV_{oi}}{X}} + \frac{sV_{oi}}{X} Ei\left(-\frac{sV_{oi}}{X}\right)$$

and

$$P_e = \int_{V_{oe}}^{\infty} \frac{V - V_{oe}}{V} F(V)dV = e^{-\frac{sV_{oe}}{X}} + \frac{sV_{oe}}{X} Ei\left(-\frac{sV_{oe}}{X}\right),$$

where $s = (1 + P_i)\nu_i + 2P_e\nu_e$ and $Ei(\ )$ denotes the exponential integral.

But $\alpha = P_i\nu_i + P_e\nu_e$, whence

$$\alpha = \nu_i\left[e^{-\frac{sV_{oi}}{X}} + \frac{sV_{oi}}{X} Ei\left(-\frac{sV_{oi}}{X}\right)\right] + \nu_e\left[e^{-\frac{sV_{oe}}{X}} + \frac{sV_{oe}}{X} Ei\left(-\frac{sV_{oe}}{X}\right)\right]. \quad (39)$$

The type (elastic or inelastic) of variation of α with X depends on the relative magnitudes of the two terms in s. For example, in the case of argon or helium containing a trace of nitrogen or oxygen we can easily predict the general shape of the $\alpha - X$ curve. Since V_{oi} is considerably smaller than V_{oe}, P_e becomes negligible in comparison with P_i when X

[1] E. W. B. Gill and F. B. Pidduck, *loc. cit.*

[2] PHYS. REV., April, 1916.

is very small. Thus for small values of X the gaseous mixture shows the characteristics of its inelastic component. When X is large, however, P_e and P_i do not differ so greatly and the mixture has more nearly the characteristics of the gas which is present in the greater quantity. Though the relative effect of the inelastic constituent is always large in comparison with the proportion of this constituent present, the relative importance of this inelastic constituent diminishes as X increases. Fig. 5 illustrates this point. The upper curve refers to a pure elastic gas, the lower curve to a pure inelastic gas and the intermediate curve represents equation (39) for the elastic gas with a small proportion of the inelastic gas.

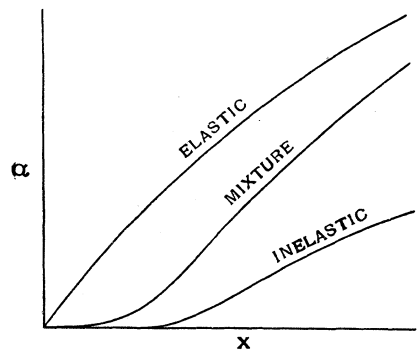

Fig. 5.

This discussion suggests the reason for the extreme electrical sensitiveness of helium and argon to the slightest traces of impurities. I have not yet succeeded in deriving an equation to replace equation (39) following the exact treatment of elastic impact given in the earlier part of this paper.

Summary.—In the first paper of this series exact expressions were obtained for the velocity distribution among the negative ions of inelastic gases and approximate expressions for this distribution in elastic gases and mixtures. These expressions applied to cases of ionization exclusively by impacts of negative ions and also to ionization by both negative and positive ions.

In the second paper an expression was derived for α, the number of new ions formed by inelastic impacts of a negative ion in a centimeter path and this expression was found to receive good experimental support.

In the present paper the functional relation between α, X and p for elastic impacts was derived and an equation for α was obtained which conformed to the best experimental data. The departure of some experimental data from this theory was shown to arise from the use of impure gases.

In all the discussion it has been assumed that velocities due to thermal agitation are negligible and that no complex ions or clusters are formed within the range of electric fields and gas pressures employed in experimental tests. The only experimental data used were those in which the effect of the finite distance between the electrodes could be neglected.

Palmer Physical Laboratory,
Princeton, N. J.