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THE THEORY OF IONIZATION BY COLLISION.

II. Case of Inelastic Impact.

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IN the preceding paper[1] an investigation was made of the distribution of velocities among the ions in a discharge tube when the current through the gas is sufficiently small that the potential gradient may be considered uniform. Townsend[2] has shown that under these conditions α, the average number of new ions formed per centimeter path by the impacts of each negative ion (electron), may be expressed by an equation of the form

$$\frac{\alpha}{p} = f\left(\frac{X}{p}\right), \tag{23}$$

where X is the potential gradient and p the pressure. This relation has been supported by all experiments with gases in which the impacts of electrons with gas molecules are inelastic, *i. e.*, when the electron loses its kinetic energy at each collision.

Various assumptions regarding the mechanism of ionization by collision have led to various forms of the function f. Townsend,[3] assuming that ionization always occurs at an impact when the electron has moved through a potential drop exceeding the minimum value V_0, derived the equation

$$\alpha = \nu e^{-\frac{\nu V_0}{X}}, \tag{24}$$

where ν is the average number of collisions with gas molecules made by each electron in a centimeter path. By assuming arbitrary values of the constants ν and V_0 for each gas this equation may be made to fit the experimental results, but the values of the constants so chosen are

[1] Phys. Rev., April, 1916.

[2] Ionization of Gases by Collision, p. 17.

[3] *Ibid.*, p. 22.

at wide variance with the values which have been determined directly. Recognizing this, Townsend has recently[1] suggested that V_0 in his equation be considered as the average rather than the minimum ionizing potential. Under these conditions equation (24) must be considered largely as an empirical equation.

Much more satisfactory is the relation derived by Bergen Davis[2] on the assumption that ionization occurs at an impact whenever the electron possesses a velocity whose component normal to the surface of the molecule (considered spherical) exceeds the minimum value corresponding to V_0. This equation is

$$\alpha = \nu \left[e^{-\frac{\nu V_0}{X}} + \frac{\nu V_0}{X} Ei \left(- \frac{\nu V_0}{X} \right) \right], \tag{25}$$

where $Ei(\ )$ represents the exponential integral. It will be shown that Bergen Davis' assumptions really require a modification of equation (25). Further discussion of this equation will appear later.

The purpose of this paper is to derive a new expression for α and to test it with such experimental data as are available. It is found to agree well with experimental results as regards both the variation of α with X and the values of V_0 for various gases.

Theory.—The two factors which determine the laws governing the production of ions by impact are the distribution of velocities among the colliding electrons and the function of the velocity which represents the probability that an electron will ionize at an impact. Thus if $F(V)dV$ represents the probability that an electron has fallen through a potential drop between V and $V + dV$ and if $f(V)$ represents the probability that an electron with a velocity V ionizes when it collides, then $f(V)F(V)dV$ is the probability that an electron will possess a velocity corresponding to V and will ionize when it collides. Thus

$$P = \int_0^\infty f(V)F(V)dV$$

is the probability that any electron, chosen at random, ionizes when it collides. This quantity, when multiplied by ν, is equal to α.

$F(V)dV$ is given by equation (7) of the preceding paper.[3] As to the form of $f(V)$, we know that $f(V) = 0$ when $V \leqq V_0$ and that it must approach the value unity when V is large. The simplest form of such a function is one which fits the facts as far as we know them; we shall therefore assume that

$$f(V) = \frac{V - V_0}{V} \quad \text{when} \quad V \geqq V_0. \tag{26}$$

[1] Electricity in Gases, p. 295.
[2] PHYS. REV., 24, p. 93, 1907.
[3] *Loc. cit.*

This relation is essentially the same as that which follows from Bergen Davis' assumption regarding the necessary condition for ionization at an impact. It may be correct, however, even if the interpretation given by Bergen Davis is not true. The bearing of certain experiments by Glasson[1] on this point will be discussed later.

If we make these substitutions in the equation for P we obtain

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

of which the solution is

$$P = e^{-(1+P)\frac{\nu V_0}{X}} + (1 + P)\frac{\nu V_0}{X} Ei\left(- (1 + P)\frac{\nu V_0}{X}\right),$$

where $Ei(\ )$ denotes the exponential integral. Thus we find

$$\alpha = P\nu = \nu \left[e^{-(1+P)\frac{\nu V_0}{X}} + (1 + P)\frac{\nu V_0}{X} Ei\left(- (1 + P)\frac{\nu V_0}{X}\right)\right], \quad (27)$$

which conforms to equation (23) since ν is proportional to p.

Discussion of Equation.—Equation (27) differs from the expression given by Bergen Davis by the presence of the factor $(1 + P)$ whose omission from his equation results from neglecting to consider the effect of the newly formed ions on the velocity distribution.

It is impossible to solve equation (27) for α or P explicitly. However P may be found in terms of $(1 + P)(\nu V_0/X)$ (see Làska's "Sammlung von Formeln"), from which I have computed the following table of values:

TABLE I.

P	$\frac{\nu V_0}{X}$	P	$\frac{\nu V_0}{X}$	P	$\frac{\nu V_0}{X}$	P	$\frac{\nu V_0}{X}$
0.00099	5.00	0.0731	1.446	0.3893	0.2880	0.725	0.0580
0.0032	3.99	0.1485	0.872	0.518	0.1645	0.804	0.0333
0.0106	2.97	0.2008	0.666	0.574	0.1271	0.854	0.0216
0.0375	1.963	0.2762	0.4705	0.656	0.0846	1.000	0.0000

In order to test equation (27) P was plotted as a function of $\nu V_0/X$, whence P, and therefore α, could be determined graphically for any given value of $\nu V_0/X$.

Comparison with Experiment.—(*a*) *Variation of α with X.*—Numerous experiments on the variation of α with X in various gases contained between parallel plate electrodes afford a means of testing equation (27). Of the available data, those for nitrogen, carbon dioxide, hydrochloric acid and water vapor are found to be in excellent agreement with equation

[1] Phil. Mag., 22, p. 647, 1911.

(27). In helium, argon and hydrogen the collisions are entirely or partly elastic and equation (27) cannot be applied. They will be considered in a subsequent paper.

In selecting experimental data I have taken the results of the most recent, or otherwise apparently most reliable, experiments on each gas. All results which are appreciably affected by the error in such measurements pointed out by Farwell,[1] or for which there is an appreciable difference between the velocity distributions given by equations (8) and (10) of the preceding paper, have been rejected. In view of the labor of gathering and testing the available data it may be of value to include them here. The data given in Table II. have been reduced by equation (23) so as to apply to a pressure of 1 mm.

TABLE II.

$p = 1$ mm.

N_2[2]		CO_2[3]	
X	α	X	α
43.75	0.021	87.5	0.62
87.5	0.337	175	2.32
131	0.96	350	5.65
175	1.77	700	10.64
262	3.59	875	11.83
350	4.42	1050	12.68
525	6.41		
H_2O[4]		HCl[5]	
32.5	0.02	55.5	0.12
54	0.29	68.5	0.41
65	0.57	69	0.36
97.5	1.25	103	1.10
103.5	1.41	104	1.38
107.5	1.56	112.5	1.36
134	2.25	116	1.66
163.5	2.80	138	2.30
205	3.79	172	3.38
221	4.08	203.5	4.23
307	5.49	232	5.08
374	6.23	305	6.96
		357	8.00
		407	9.18
		535	11.20
		715	13.40

[1] PHYS. REV., 5, p. 149, 1915.
[2] H. E. Hurst, Phil. Mag., 11, p. 535, 1906.
[3] *Ibid.*
[4] J. S. Townsend, Phil. Mag., p. 389, 1903.
[5] *Ibid.*

The exactness with which equation (27) conforms to these data is indicated by Fig. 2. The solid curve in each case represents the graph of equation (27), the constants ν and V_0 being chosen to give the best agreement between the curve and the data. I find that equations (24)

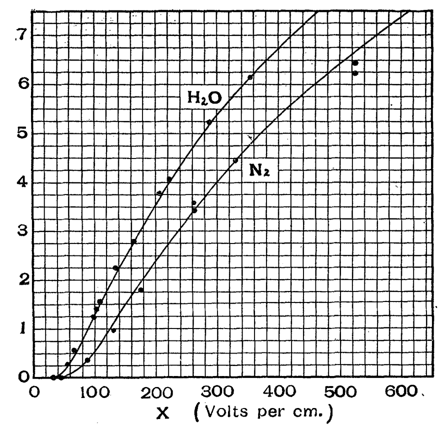

Fig. 2(*a*).

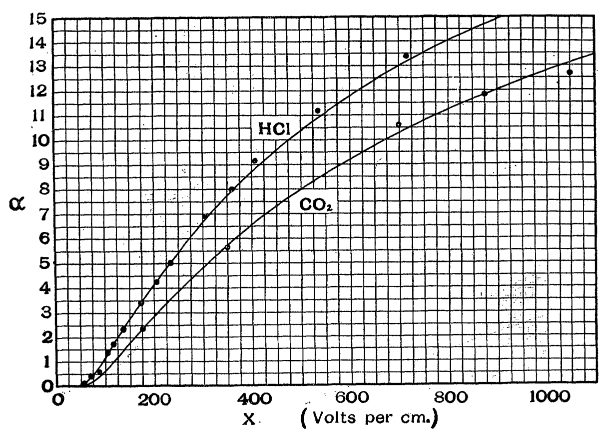

Fig. 2(*b*).

and (25), for Townsend's and Bergen Davis' theories, agree nearly, though not quite, as well as the present theory. Possibly all are within the limits of experimental error. But when the values of the constants necessary to bring this agreement are compared with the results of direct measurements there is evident support of the present theory.

Values of V_0.—The minimum ionizing potential V_0 for a few gases has been measured directly by Franck and Hertz[1] and by Pawlow.[2] Their values are given in Table III. in the column marked *Exp.* In their

TABLE III.

Values of V_0.

	Exp.	Exp.*	Equation (27).	Townsend.	Davis.
N_2	7.5	10.0	10.05	27.5	12.36
CO_2			8.2	23.3	9.63
H_2O			7.47	22.4	8.98
HCl			6.05	16.5	7.30
He	20.5	22.5	22.5	12.3	5.6

experiments the source of electrons was a hot filament, from which the electrons escape with a definite velocity distribution. Pawlow determined this distribution and found that the fastest electrons which he could detect escaped with an initial velocity corresponding to about 2.5 volts. Now as the accelerating potential is raised ionization will first be noticed when these fastest electrons acquire the minimum ionizing velocity. Apparently, however, this initial velocity has not been included in the published values of V_0. It appears to me, therefore, that these values should each be increased by about 2.5 volts. These revised values are placed in the column marked *Exp**. In the remaining columns are given the values of V_0 which cause the curves representing the three theories to accord best with the data in Table II. I have also anticipated the results of the following paper and included the value of V_0 for the elastic gas helium, since the theoretical treatment is exactly the same as in the present paper except for the effect of elastic impact. The results for hydrogen have not been included since in this case impact appears to be partly but not wholly elastic and I have not been able to solve the equation for such a case. Townsend's and Davis' equations do not really apply to the case of elastic impact, and the value for helium calculated from these equations has been included in order to illustrate the important fact that when applied to cases of elastic impact they tend to give values of V_0 which are too small. Since for nitrogen they give values of V_0 which are too large it is not likely that the impacts in nitrogen are elastic enough to make the present treatment appreciably in error.

Where comparison with direct experiment is possible the present theory is seen to fit the facts most acceptably. In fact, if the suggested correction of the experimental data is true, the agreement is almost exact. It is unfortunate that comparison is possible in so few cases. It is known

[1] Verh. d. D. Phys. Ges., 16, p. 457, 1914. [2] Roy. Soc. Proc., 90, p. 398, 1914.

however, that CO_2, H_2O and HCl may be ionized with comparative ease and to this extent there is support of the theory.

Another possible test of these values of V_0 is afforded by photoelectric experiments in which the minimum ionizing potential for a gas may be calculated from the maximum wave-length of light which can ionize the gas. These wave-lengths, however, are so extremely short that no accurate data are available and it can only be said that no existing evidence of this sort casts doubt on the values of V_0 given by the theory.

Bergen Davis[1] has recently modified his equation to apply to the experimental arrangements employed by Franck and Hertz and has found good support of his equation in their experimental data. It is to be noted that their measurements were carried on under conditions in which the factor $(1 + P)$ which appears in equation (27) does not need to be considered, whence the formulæ in Bergen Davis' and the present theories become identical. Unfortunately the lack of a source of electrons of homogeneous velocities complicates the interpretation of such results.

Values of ν.—Another test of the relative merits of the theories is afforded by a comparison of the calculated values of ν with those determined experimentally. From the assumptions underlying the theories ν, for inelastic impact, should equal $\pi R^2 N$, where N is the number of molecules per unit volume and πR^2 is that part of the molecular cross section which is effective in stopping the impinging electrons. In Table IV. I have included the values of ν calculated from the three theories and also calculated on the assumption that R is the known molecular radius.[2]

Table IV.

Values of v for $p = 1$ mm.

Gas.	$\pi R^2 N$	Equation (27).	Townsend.	Davis.
N_2	34.5	22.5	12.4	17.6
CO_2	49.5	30.0	20.0	23.2
H_2O	47.0	21.7	12.9	15.7
HCl	46.0	33.3	22.2	26.8
He	13.5	10.0	2.8	3.05

Evidently the part of the molecular cross section which is effective in stopping the electron is less than that which functions in collisions of molecules with each other. One cannot speak very definitely about this point since the meaning of a collision is not entirely clear in either case.

[1] Phys. Rev., p. 118, 1915.

[2] Kaye and Laby's Tables.

An interesting hypothesis is this: that the explanation of the above results is to be found in the discrete structure of the molecule, for it is conceivable that a rapidly moving electron might penetrate a molecule without colliding with any of its constituent parts. If this explanation is correct, the ratio of the actual values of ν to the values of $\pi R^2 N$ in Table IV. would represent the probability that an electron could not pass through the space occupied by a molecule without colliding with some of its constituent parts.

Glasson has found[1] that, with very high velocities, the number of ionizing collisions per unit path by an electron *decreases* as the velocity increases, which is contrary to what we might expect. In line with the suggestion just made, it is likely that Glasson's results are not due to a decrease with velocity in the probability of ionization at a collision, but rather to an actual decrease in the number of collisions. In other words, we may consider ν to be a function of the velocity such that ν decreases at very high velocities. Direct evidence of this is afforded by the photographs of paths of β particles through gases. The reason appears to be that a molecule has a discrete structure and that an electron has the best chance of getting through freely when its velocity is large compared with the velocities of the constituent parts of the molecule in their orbits. Such a view removes an apparent objection to equation (26).

However this may be, no test of the ionization theories by considerations of ν can be made at this time owing to the lack of experimental measurements of ν. Such measurements are now being attempted in this laboratory.

Further support of the assumptions underlying equation (27) will appear in a following paper on the subject of elastic impact.

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[1] *Loc. cit.*