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REACTION EFFECTS PRODUCED BY THE DISCHARGE OF ELECTRICITY FROM POINTS IN GASES AND THE BEARING OF THESE EFFECTS ON THE THEORY OF THE SMALL ION.[1]

By Edward J. Moore.

ARRHENIUS[2] published in 1897 a series of observations on the reaction effects produced when electricity discharges from points in gases. He found that the ratio of the reaction to the current was very nearly constant and that the force of reaction was approximately inversely proportional to the pressure when the current was constant.

His results are discussed by J. J. Thomson[3] from the standpoint of the electron theory and the following equation developed for the force of reaction on the point:

$$F = \frac{i}{K}\int dz, \qquad (1)$$

where i is the current, z the direction of the normal from the point to the plane and K the velocity of the ion in unit field. This equation assumes that ions of one sign only are present in the region between point and plane, that these ions are formed in the immediate neighborhood of the point, and travel without change in character to the plane opposite. It seems improbable, as Thomson himself points out, that both these conditions are strictly fulfilled in practice. This investigation was undertaken in order to see to what extent the above relations would hold under the experimental condition that must be imposed. It was hoped that even if the method did not prove to be capable of yielding satis-

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[1] A preliminary report of this paper was presented at the Minneapolis meeting of the Physical Society, December, 1910.

[2] Wied. Ann., Vol. 63, p. 305, 1897.

[3] Conduction of Electricity through Gases, 2d ed., p. 507.

factory results for the absolute values of the mobilities it would, nevertheless, yield consistent relative values and in that way, serve to throw light on the interesting and much discussed question of the character of the gaseous ion.

The Apparatus and the Method.

Two forms of the apparatus were used. The arrangement was very simple. In the first form two fine sewing needles were fastened to a wire and formed into a couple (see Fig. 1). This couple was suspended by a phosphor bronze ribbon in such a way that electricity could be made to discharge from the points to the planes P and P' placed opposite. These planes were five cm. in diameter and were connected to earth through a galvanometer G, Fig. 2. The distance z between point and plane could be varied between 0 and 5.5 cm. The position of the couple could be read by means of the mirror M. The force of reaction for a given value of z could be measured by the torsion of the suspension, and at the same time the current flowing from the points could be measured by the galvanometer. The apparatus was placed under a large bell jar and arranged so as to admit of varying the pressure. The inside of the bell jar was covered with tin-foil and connected to earth. Electrical connection with the points was effected through a stop cock T in the top of the bell jar. This stop cock served also as a torsion head for measuring the reaction.

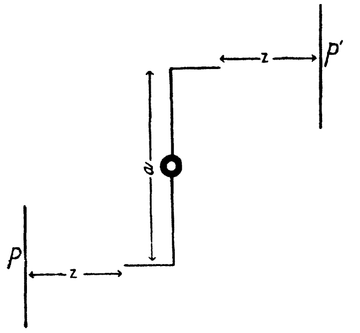

Fig. 1.

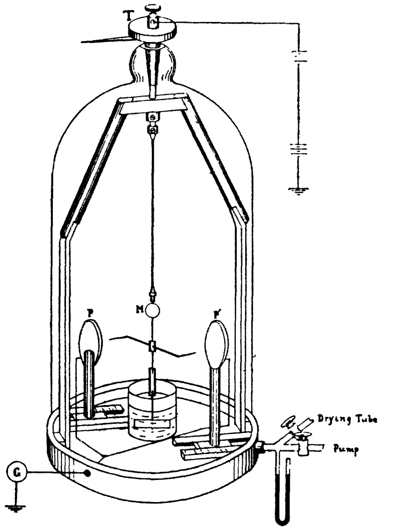

Fig. 2.

The second form differed from the first in having, as it were, two couples (see Fig. 3) instead of one. The planes were replaced by a cylindrical brass ring 18 cm. in diameter and 5 cm. wide. The ring was connected to earth through the galvanometer and observations were made in precisely the same way as with the single couple. This form of the apparatus was well adapted for measuring the mobility with varying pressures, and yielded curves identical in form with those obtained with the single couple. An aluminum vane, connected to the couple by a piece of ebonite and dipped into a vessel of oil, served to damp the couple.

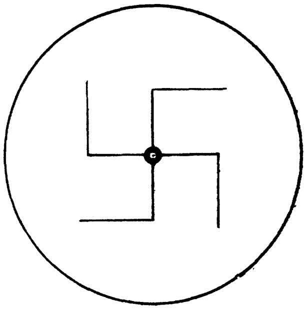

Fig. 3.

The galvanometer was of the ordinary D'Arsonval type. One centimeter deflection at a distance of 2 meters corresponded to 1.9×10^{-8} amperes.

A constant source of potential was obtained from small storage batteries. 10,000 volts were available. Without this constant source this investigation could not have been successfully carried out, especially at the lower pressures, where a variation of a few volts produced a large variation in the current.

The equation of the couple is

$$Fa = T_0\theta, \tag{2}$$

where F is the reaction on the point due to the ions in the gas streaming from it, a is the couple arm, T_0 the torsion constant and θ the angle of twist in radians. Substituting this in equation (1) we have

$$\theta = \frac{ai}{T_0K}\int dz. \tag{3}$$

Observations were made in the following way. The zero position of the couple was first observed with a telescope and scale. A potential was then applied to the points and the torsion head turned to keep the couple in the zero position. In this way the potential was varied until the desired current was obtained. The values of the current and the torsion were then noted. Owing to the fact that the current, the reaction, the distance between the points and the planes and the potential all varied simultaneously, it was not easy to duplicate conditions in consecutive readings. However, the results of these observations seldom differed among themselves by more than two or three per cent.

If a charge q is placed at a distance d from an infinite plane AB maintained at zero potential the density of the induced charge on the surface of AB is inversely proportional to the cost of the distance, *i. e.*, $\sigma = \alpha/r^3$.

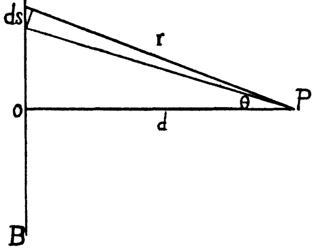

Fig. A.

Correction for electrostatic attraction between the point and plane.

The total charge on the plane will be

$$\int \sigma ds \qquad (a)$$

but

$$ds = r^2 \frac{dw}{\cos\theta}.$$

From (a) we get

$$\int_0^{2\pi} \frac{\alpha dw}{d} = \frac{2\pi\alpha}{d} = q,$$

$$\therefore \alpha = \frac{qd}{2\pi} \quad \text{and} \quad \sigma = \frac{qd}{2\pi r^3}.$$

Now the pressure per sq. cm. on the plane is

$$2\pi\sigma^2 = \frac{q^2 d^2}{2\pi r^6}.$$

The total pressure

$$F = \int p ds = \frac{q^2 d^2}{2\pi} \int \frac{ds}{r^6},$$

$$q^2 \int_0^{\pi/2} \frac{\cos^3\theta \sin\theta d\theta}{d^2} = \frac{1}{4} \frac{q^2}{d^2}.$$

Since $q = CV$, the above equation becomes

$$F = \frac{1}{4} \frac{C^2}{d^2} V^2, \qquad (4)$$

which gives the relation of the attraction between point and plane in terms of the applied potential and the distance. All the observations on the reaction produced on the point by a discharge from it had to be corrected for this force, which of course was of opposite sign to the force of reaction. The method of making this correction was to observe the attraction between point and plane, using equation (2), as the potential was increased up to the point where a current began to flow. These attractive forces F were plotted with F as ordinates and PD as abscissas and the equation of the experimental curve determined in the following way. Assuming that the equation of this curve was of the form of equation (4), viz.,

$$v^n = PF,$$

then

$$n \log V = \log P + \log F,$$

replacing $\log V$, $\log P$ and $\log F$ by $V'P'$ and F' we have

$$F' - nV' + P' = 0.$$

Since F' and V' are numbers obtained from the experimental curve they can be plotted. The result should be a straight line. From this line n and P can be found. Fig. 4 shows typical curves of this kind obtained for different couples. The equation of the first is

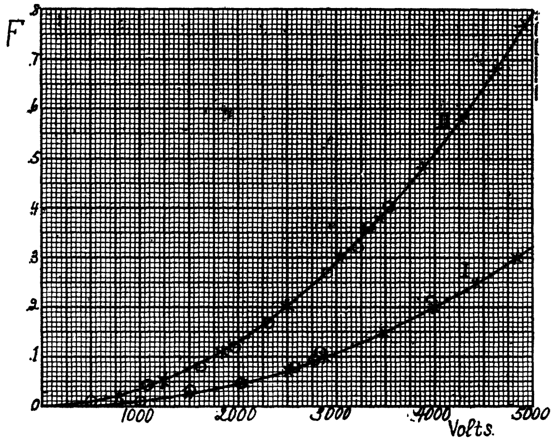

Fig. 4.

$$V^{2.060} = 1.3 \times 10^8 F,$$

the second,

$$V^{1.971} = 2.47 \times 10^7 F.$$

Circles indicate observed points and crosses points calculated from the equations of the curves. The equations of a large number of these curves were determined and the values of the exponent of V were all within the limits of those given in the above equations. By extrapolating on these curves the values for the correction at the higher potentials were obtained.

RESULTS AT ATMOSPHERIC PRESSURE.

The curves in Figs. 5 and 6 were found by first determining the equation for the attraction at the different values of z and then measuring the reaction at these points. Fig. 5 shows the results obtained when i is constant and z varied. Fig. 6, the results when z is constant and i varied. The experimental points are not mean values but single observations. When one considers the number of variables that must be controlled in making an observation these points lie fairly close to the straight line which equation (3) would require.

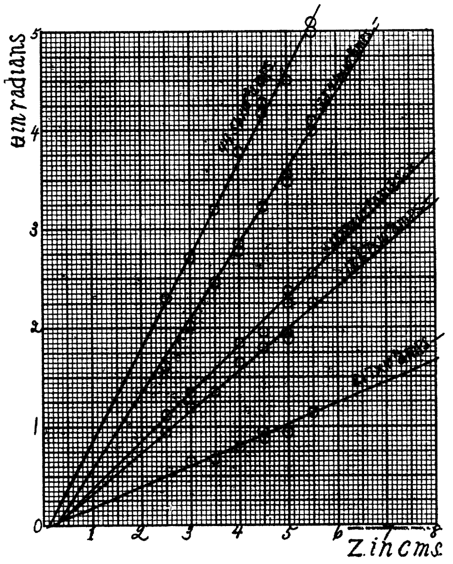

Fig. 5.

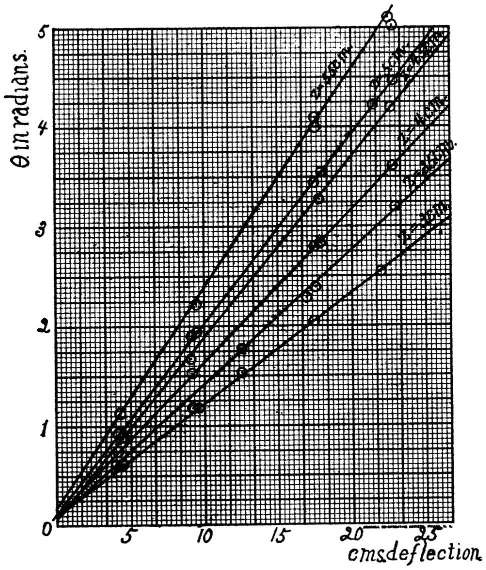

Fig. 6.

According to equation (3), therefore, the slopes of the lines in Fig. 5 should equal ai/T_0K. Since we know all these quantities K can be calculated at once. However, when this was tried it was found that the value of K increased with the current. The slopes of the lines in Fig. 5 were plotted with the current and the straight line of Fig. 7 was obtained. The slope of this line is a/KT_0. This gives a constant value for K and indicates that for this experiment equation (1) should be written

$$F = \left(\frac{i}{K} + C\right) \int dz, \tag{5}$$

where C is a small constant.

K computed in this way came out 9.72 cm. for the negative ions and

6.43 cm. for the positive ions. Chattock[1] by measuring the wind pressure produced by electricity discharging from a point obtained $K_- = 1.80$ cm. and $K_+ = 1.32$ cm. Zeleny's[2] values were $K_- = 1.87$ cm. and $K_+ = 1.36$ cm. Franck[3] found K_- to vary from 8.8 to 12.26 cm. and K_+ from 2.5 to 3.77 cm. when he measured his velocities over short distances close to the point in strong fields using Zeleny's method. However, when he measured the velocities over greater distances using a modification of Rutherford's method, producing his ions from point discharge, he obtained $K_- = 1.79$ cm. and K_+ 1.34 cm., values which are in good agreement with those obtained by other observers.

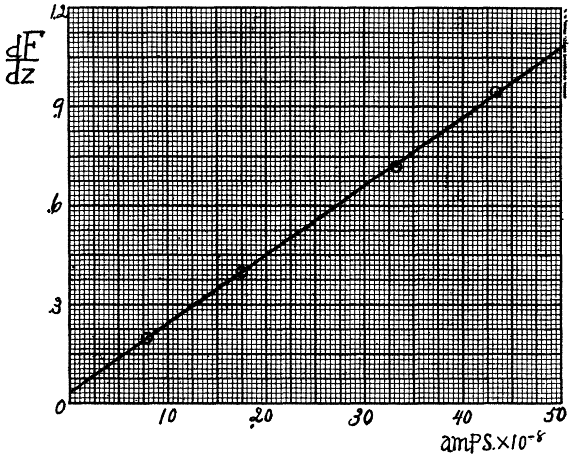

Fig. 7.

If we consider the ratio, K_-/K_+, Zeleny's[4] value is 1.37, Chattock's[5] 1.36, Franck's[6] 1.35. This work gives 1.51 or taking the inverse ratio of the reactions from the data given in the second part of this paper $K_-/K_+ = 1.49$. The average of a number of observations made using the form of the apparatus of Fig. 3 gives 1.485. If we take Kovarik's[7] value for the velocity of the negative ion and the average of the above values for the positive we get for this ratio 1.507. Thus it appears that the ratios of the mobilities obtained from the reaction effects are in fair accord with those given by other methods, while the absolute values are very much too high. The following considerations may in

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[1] Chattock, Phil. Mag., Series 5, 48, 1899.

[2] Zeleny, Phil. Trans. A., Vol. 195, p. 193, 1900.

[3] Franck, Ann. d. Phys., 4, Vol. 21, p. 972, 1906.

[4] Loc. cit.

[5] Loc. cit.

[6] Loc. cit.

[7] Kovarik, PHYS. REV., Vol. 30, p. 415, 1910.

part account for these discrepancies. Franck's work indicates that the velocity is very much higher near the point than it is farther out. Tyndall[1] concludes that whatever clustering there is, in air at atmospheric pressure, occurs immediately after the formation of the electron, *i. e.*, the electron does not travel an appreciable distance before it becomes attached. Now, if the ionization in the case of the negative begins farther from the point than in the case of the positive, and this is a most reasonable assumption, the method used by Franck would give a large difference in the apparent velocities. The mobility as calculated from equation (5) depends upon dF/dz. If this is cut down in any way the apparent value of K is increased. If we assume that the gas is ionized for some distance from the point and that the region of ionization extends farther out as z is increased, which is reasonable, as the field increases with z, the ions of opposite sign traveling back to the point would tend to reduce the value of dF/dz. If we assume also, that there is back discharge, *i. e.*, ions of opposite sign traveling from the planes to the points, and assume further that this back discharge increases as z increases, we have another very important factor in cutting down the value of dF/dz. Many observers have found back discharge, and Chattock and Tyndall[2] point out that in their experiments it increased with z. Zeleny[3] finds the back discharge greater for positive ions traveling from point to plane than for negative. If this is a correct view of the mechanism of point discharge large values of K would be expected from this method.

Another possible effect upon the reaction might be a forward drag upon the points due to the air currents set up in the gas by the moving ions. Such a drag, if it existed, would be directly proportional to the area of the points. Points whose area varied in the ratio 1, 2, 3 and 4 were used. The results showed that if such an effect existed it was negligibly small. This also tends to confirm the view that ionization begins at some distance from the point.

THE VARIATION OF MOBILITY WITH PRESSURE.

A number of experimenters have worked on this problem and have reached conclusions very much at variance with one another. Two methods have been used for this work. Rutherford[4] made the first observations in 1898, using the alternating field method. This method lends itself to measurements on the negative ion only. Rutherford

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[1] Tyndall, Phil. Mag., S. 6, Vol. 21, May, 1911.

[2] Chattock and Tyndall, Phil. Mag., S. 6, Vol. 19, p. 455, 1910.

[3] Zeleny, PHYS. REV., Vol. 33, p. 70, 1911.

[4] Rutherford, Proc. of Camb. Phil. Soc., IX., p. 401, 1898.

concluded, as a result of his work, that the mobility of a negative ion was inversely proportional to the pressure. He used pressure as low as 34 mm.

Langevin[1] devised a method which enabled him to measure the mobility of both positive and negative ions with varying pressure. His observations extended over a range of pressures from 142 cm. down to 7.5 cm. of Hg. His results indicate a marked increase in the mobility of the negative ion beginning in the neighborhood of 20 cm. of Hg., the positive showing only a tendency to increase at 10 cm. of Hg. These observations were made in air, as were also Rutherford's.

Wellisch[2] in the Cavendish Laboratory, using Langevin's method, measured the mobility of both positive and negative ions in a large number of gases and vapors. His values for the mobilities at normal pressure are in good agreement with the results obtained by other observers. He found, however, that the mobilities of both positive and negative ions were inversely proportional to the pressures. The range extended from atmospheric pressure to 1 cm. of Hg.

Kovarik[3] used a slight modification of Rutherford's alternating field method. He worked with air and CO_2 and his range of pressures extended from 760 mm. to 8.8 mm. The method limited him to observations on the negative ion and his results show a very rapid increase in the mobility at about 10 cm. pressure. This rapid increase in the velocity of the negative ion at the lower pressures has always been interpreted to mean that the negative ion at ordinary pressure is an electron with a cluster of one or more molecules attached to it. At the lower pressures according to the results of Langevin and Kovarik it simplified its character by freeing itself from some or all of the attendant molecules, thus being able to move through the gas at a very much higher velocity, whereas the results of Rutherford and Wellisch seem to indicate no such simplification. Langevin's observations on the positive indicate a tendency toward simplification below 10 cm. while Wellisch finds that it appears to persist in its original form at pressures as low as 1 cm.

In view of the lack of complete agreement in the results obtained by the methods heretofore employed for measuring the mobility with varying pressure further experiments along this line seem desirable. Notwithstanding the unsuitability of the present method to the problem of a correct determination of the absolute value of K, the above observations would seem to indicate that it would probably yield consistent values

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[1] Langevin, Ann. de Chemie et de Physique, t. XXVIII., p. 289, 1903.

[2] Wellisch, Phil. Trans., A., Vol. 209, pp. 249–279, 1909.

[3] Loc. cit.

for the variation of the mobility with varying pressure and if so, would be admirably adapted to throw light upon the disputed point regarding the change in the character of the ion at low pressure, since fairly accurate observations on the reaction could be obtained at lower pressures and in stronger fields than those at which it had been found possible thus far to measure mobilities. The results reached below tend to confirm this inference. Also observations made at 40 cm. pressure, when reduced to 76 cm. on the assumption that PK = constant, agreed well with values of K obtained at atmospheric pressure.

The arrangement of the apparatus was similar to that shown in Fig. 2. The pressure was measured with a mercury manometer which could easily be read to one tenth millimeter. The error in reading the pressure was well within the limits of the other errors of the experiment. The distance between the points and the planes was kept constant at 5.3 cm. Since it had been shown that for a given value of z, K is constant when i is constant, the observations were made with approximately constant currents and the value of K was obtained as follows from (1) and (2):

$$\frac{T_0\theta}{a} = F = \frac{i}{k}\int dz, \quad \therefore \quad K = \frac{i}{\theta} x \text{ constant.}$$

Assuming the law $K_0P_0 = KP$, we get

$$K_0 = \frac{Pi}{P_0\theta} x \text{ constant.}$$

The values of K_0 obtained in this way were plotted as abscissas with P as ordinates. If the mobility is inversely proportional to the pressure this should give a straight line.

Observations were made in air, hydrogen and CO_2. The pressure was varied from 760 mm. down to 5 mm. of Hg. The gases used were first thoroughly dried by passing them over calcium chloride and phosphorus pentoxide. Commercial CO_2 was used. The hydrogen was obtained by decomposing zinc with HCl in a Kipp generator. In order to remove oxygen and other impurities it was passed through pyrogalic acid and KOH, then through the drying tubes and finally admitted to the observation apparatus. The usual precautions were taken to free the apparatus from traces of air when filling it with the gas to be used.

RESULTS AT REDUCED PRESSURES.

Figs. 8, 9 and 10 show the type of variation obtained. The negative curves in air and CO_2 begin to show an increase in the mobility of the ion, over that which the law PK = constant would require, at about 20 cm. pressure. At 10 cm. there is a decided bend in the curve and as the pressure is still farther reduced the mobility increases enormously. The curves for hydrogen show the same characteristics except that the increase begins at a higher pressure and the decided bend occurs at about 20 cm. Very high velocities are reached by the time the pressure is reduced to 8 cm. The hydrogen curve indicates a tendency for the mobility to increase from the beginning. This may be due to the back discharge[1] which is so prominent in hydrogen.

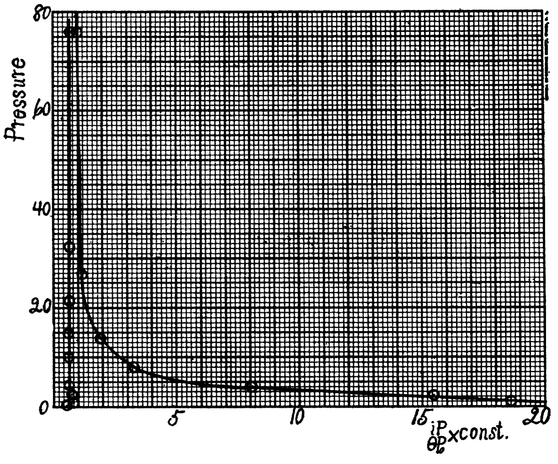

Fig. 8.

Air.

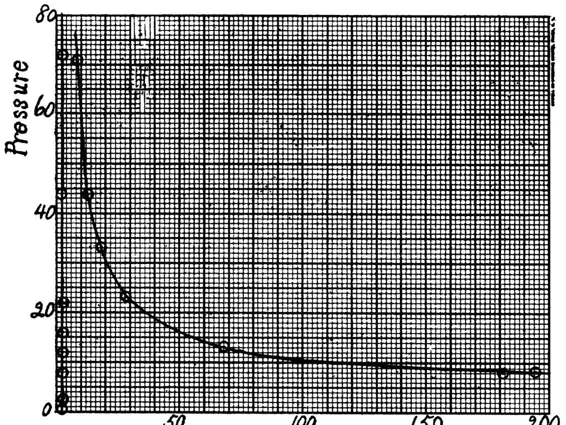

Fig. 9.

Hydrogen.

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[1] Chattock and Tyndall, Phil. Mag., Series 6, Vol. 19, p. 454, 1910; Tyndall, **Phil. Mag.**, S. 6, Vol. 21, p. 585, 1911.

Fig. 11 shows the kind of accuracy that can be obtained from this method of measurement. The observations for the points marked with crosses were made three or four days after those for the points marked with circles. In the meantime the apparatus was repaired and refilled with CO_2.

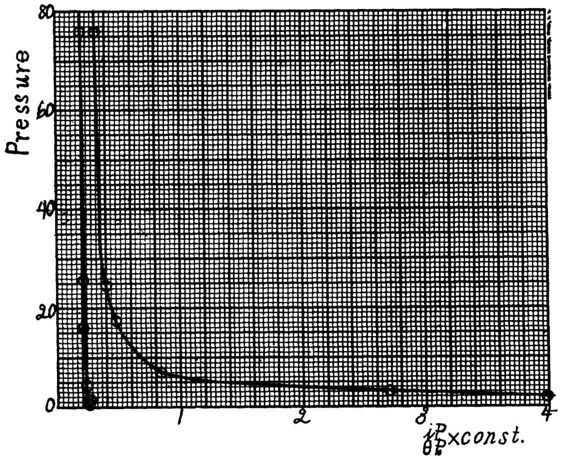

Fig. 10.

CO_2.

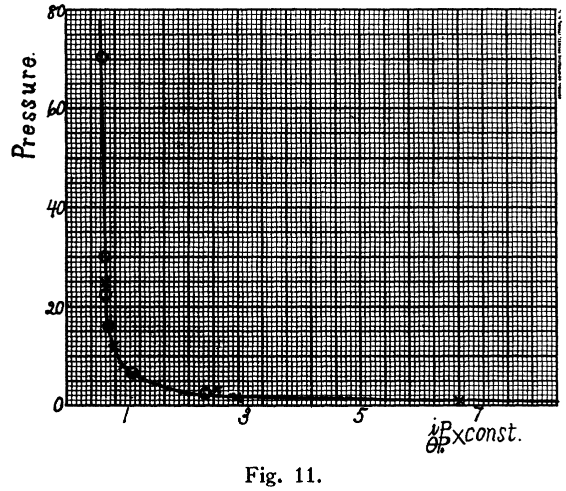

Fig. 11.

CO_2.

Tables I., II. and III. will serve to indicate the character of the data obtained by these observations.

TABLE I.

AIR.

Positive.

i Amperes.	P.D. Volts.	θ Observed.	θ Corrected.	P Cms.	$\frac{iP}{\theta P_0} \times$ Const.
12.7×10^{-7}	4,560	5.883	6.139	32.53	.749
12.0×10^{-7}	3,700	3.839	4.007	21.17	.716
12.3×10^{-7}	3,300	2.858	2.997	14.95	.684
12.3×10^{-7}	2,870	1.857	1.958	10.09	.709
12.6×10^{-7}	2,500	1.337	1.387	7.19	.729
12.3×10^{-7}	1,970	.658	.705	4.01	.779
12.2×10^{-7}	1,500	.303	.331	2.01	.797
12.2×10^{-7}	1,170	.125	.142	.85	.820
12.5×10^{-7}	1,070	.088	.092	.52	.794
Negative.					
10.5×10^{-7}	4,000	4.533	4.729	40.70	1.019
10.15×10^{-7}	3,100	2.525	2.643	27.00	1.164
10.7×10^{-7}	2,190	.867	.926	14.18	1.855
11.25×10^{-7}	1,490	.274	.301	8.01	3.34
11.8×10^{-7}	1,000	.0573	.0698	4.26	8.06
10.7×10^{-7}	725	.0112	.0167	2.17	15.56
10.0×10^{-7}	720	.00101	.0065	1.12	18.75

TABLE II.

HYDROGEN.

Negative.

i Amperes.	P.D. Volts.	θ Observed.	θ Corrected.	P Cms.	$\frac{iP}{\theta P_0} \times$ Const.
21.6×10^{-7}	2,940	1.975	2.081	71.28	8.29
22.6×10^{-7}	1,960	.736	.883	44.72	12.39
22.6×10^{-7}	1,580	.4084	.439	33.43	19.22
22.2×10^{-7}	1,180	.195	.213	23.88	28.11
23.8×10^{-7}	890	.0426	.0524	13.51	68.70
22.6×10^{-7}	800	.0382	.0462	8.27	181.3
Positive.					
				71.70	2.30[1]
12.05×10^{-7}	3,160	2.500	2.622	44.53	2.28
12.4×10^{-7}	2,801	1.705	1.801	31.42	2.41
12.2×10^{-7}	2,430	1.186	1.259	22.26	2.42
12.2×10^{-7}	2,140	.8238	.899	16.54	2.51
11.8×10^{-7}	1,880	.500	.543	12.08	2.91
12.2×10^{-7}	1,560	.359	.389	8.10	2.82
12.4×10^{-7}	1,250	.188	.208	4.63	3.15
12.7×10^{-7}	980	.0875	.0995	2.18	3.02
12.5×10^{-7}	815	.0419	.0489	.89	2.63
12.9×10^{-7}	823	.0274	.0345	.51	2.14

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[1] Calculated.

TABLE III.

CARBON DIOXIDE.

Negative.

i Amperes.	P.D. Volts.	θ Observed.	θ Corrected.	P Cms.	$\frac{iP}{\theta P_0}$ x Const.
7.9×10^{-7}	——	——	16.0	70.4	.387
7.9×10^{-7}	3,800	5.035	5.21	24.48	.407
7.9×10^{-7}	3,280	3.167	3.29	17.69	.473
8.2×10^{-7}	2,000	.7365	.785	7.15	.830
8.6×10^{-7}	1,230	.1012	.1202	3.43	2.74
6.8×10^{-7}	800	.0101	.0109	.95	4.00
Positive.					
4.3×10^{-7}	4,760	5.21	5.44	25.38	.225
5.6×10^{-7}	3,500	2.959	3.009	10.8	.226
5.5×10^{-7}	2,380	1.033	1.102	4.40	.246
4.0×10^{-7}	1,750	.2304	.267	1.53	.258
5.6×10^{-7}	1,550	.063	.092	.41	.268

From these results it seems clear that whether the negative ion is a charged molecule (Wellisch's view) or a cluster of molecules (Langevin's view) it simplifies its character in the neighborhood of 10 cm. pressure for air and CO_2 and 20 cm. for hydrogen; on the other hand, whatever the character of the positive ion it remains unchanged at the lowest pressures observed.

Since this work was completed (September, 1910), and presented to the American Physical Society (December, 1910), a paper has appeared by Todd[1] which gives the results which he has obtained by so modifying Rutherford's method as to make it possible to use it in measuring the mobility of positive ions at reduced pressure.

Todd's results are in complete agreement with those found above, in that the law PK = constant holds for positive ions at pressures as low as 1 mm.

CONCLUSIONS.

1. The relation between the force of reaction and the distance between point and plane in point discharge has been investigated and found to be linear within the range of currents and distances used. The relation between the force and the current for different values of the distance was also found to be linear. The experimental relation is expressed by the equation

$$F = \left(\frac{i}{K} + C\right)\int dz.$$

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[1] Camb. Phil. Soc. Proc., 16, p. 21, February, 1911.

2. The absolute values of the velocities of the ions in unit field were found to be very much higher than those obtained by other methods. The ratio of the velocities, however, was only slightly higher. A possible explanation of the high velocities is suggested.

3. The variation of the mobility with pressure has been measured from 760 mm. to 5 mm. pressure in air, hydrogen and CO_2. The mobility of the positive was found to be inversely proportional to the pressure in all cases down to 5 mm. The negative ion showed a rapid increase in mobility, beyond that required by the law PK = constant, beginning at about 20 cm. Below 10 cm. the mobility became very large. In the case of hydrogen these effects occur at somewhat higher pressures.

Before concluding the author wishes to thank Professor A. A. Michelson and the members of the Ryerson staff for their interest and encouragement, especially Professor R. A. Millikan, at whose suggestion this investigation was undertaken, and who has offered many helpful suggestions during its progress.

Ryerson Laboratory,
University of Chicago.
August, 1911.