THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

NOVEMBER 1899.

XLIV. *On the Velocity and Mass of the Ions in the Electric Wind in Air.* By A. P. CHATTOCK, *Professor of Physics, University College, Bristol**.

IT is a generally accepted theory of what happens when a sharp point discharges electricity through a non-conducting gas onto a smooth metal plate, that the strong field at the point dissociates the gas into + and - ions, and that a one-way flow of the ions of like sign to the point thereupon ensues from point to plate.

Rutherford (*Phil. Mag.* Nov. 1897) has measured the velocity of ions dissociated in gases by Röntgen and by uranium rays, and finds that for air the sum of the + and - velocities in a field of one volt per centimetre is 3.2 centimetres per second. Zeleny (*Phil. Mag.* July 1898) has since shown that the ratio of the velocity of the negative to that of the positive ions in the same field is 1.25 for air.

One object of the present paper is to show that the ions dissociated at a sharp point in air are probably identical with those studied by Rutherford and Zeleny.

Theory of the Method.

Let B, fig. 1, be a sharp positively electrified metal point in a non-conducting gas, opposite and at distance z from an

* Communicated by the Author. A small portion of this paper was read at the Bristol Meeting of the British Association last year.

infinite earth-connected flat metal plate A ; and x and y two infinite planes parallel to A and distant apart dz .

da is a small area on x , and the arrow F represents the field at da , θ being the angle between F and the normal to x .

ρ is the volume-density of the + ions in the element $da \cdot dz$.

C is the whole current passing from B to A; dC the current through da ; both in electrostatic units.

V is the velocity of the ions in unit electrostatic field relatively to A.

If it be assumed that the motion of the ions is viscous, and that their velocities are very great compared with any motion of the gas as a whole,

$$dC = \rho V F \cos \theta da. \quad . \quad . \quad . \quad . \quad . \quad . \quad (i.)$$

The passage of the ions through the gas is accompanied by a drag on the latter which, if the ions move with uniform velocity, is equal to the product of their charges and the strength of the field : hence if d^2p be the component of the drag in element of volume $da \cdot dz$ resolved normal to A,

$$d^2p = \rho F \cos \theta da dz. \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii.)$$

Combining (i.) with (ii.)

$$V = dC dz / d^2p. \quad . \quad . \quad . \quad . \quad . \quad . \quad (iii.)$$

Since V and dz are constant for the planes x and y it follows that dC/d^2p is constant, and that we may therefore replace this ratio by C/dp , where dp is the total drag on the gas between x and y normal to A. Then, since C is constant for all planes between A and B, dz/dp is constant, and may be replaced by z/p , where p is the total normal drag on the gas between A and B due to electrical forces only. Equation (iii.) thus becomes

$$V = Cz/p. \quad . \quad . \quad . \quad . \quad . \quad . \quad (iv.)$$

p makes itself felt as a pressure on A, and may be measured by this pressure if it is due to p alone. This, however, is not necessarily the case. If the ions possess appreciable inertia they will contribute a certain amount of pressure, π , to the gas, and through it to A, in coming to rest. Hence if P represents the total fluid pressure on A due to the current, (iv.) becomes

$$V = Cz/(P - \pi). \quad \dots \dots \dots (v.)$$

With a sharp point and gas at atmospheric pressure the ions give up the greater part of their momentum very near the point; when this is the case a curve of P plotted with z should be a straight line cutting the axis of P in π .

Experiments by "Hole in Plate" Method.

The above argument was the outcome of an attempt to interpret a series of observations made at the beginning of last year for the purpose of mapping the distribution of pressure on a flat metal plate when blown against by the electric wind. The method of experiment was as follows:—

An ebonite box E (fig. 2) was fitted with a false bottom A

Fig. 2.

of brass plate, perforated with a minute hole H (0.9 millim. diam.). H communicated by a tube, T, with a U-tube water-pressure gauge, read by a microscope, and sensitive enough

to indicate a pressure of about 0.2 dyne per sq. centim. Above A a fine platinum wire B (diam. 0.055 millim., end rounded in blowpipe) was carried by the sliding arm G, and so adjusted that when moved horizontally by G it passed exactly over the hole in A. By means of the scale S it was thus possible to measure the intensity of pressure on A when discharged against by B, for various known distances, S, between the hole and the foot of the perpendicular from B onto A; the current C received by A being also measured by connecting A to earth through a galvanometer, with special precautions to prevent electricity from passing through the galvanometer other than that received by A from B through the gas. B was arranged to slide vertically, so that the distance z between the point and A could be varied from nothing to about two centimetres; and the metal disk D could be moved up or down upon the support of B. The edge of D was bound with sheet indiarubber to prevent it from discharging.

The plate close round H was divided into a series of three concentric metal rings (not shown in the figure) which were insulated from one another by ebonite, and of which the mean diameter of the outermost insulation was about 3.3 millim. These rings could be connected separately or with the rest of A to the galvanometer, and were for the purpose of determining the distribution of the current on A simultaneously with the distribution of pressure. As the insulation which separated the rings was less than 0.2 millim. wide, the continuity of A was hardly affected by their presence.

Curves I. and II. are typical of the results obtained with this apparatus. In each case the abscissæ are the values of S (fig. 2); the full curves being for positive discharge, the dotted for negative. d is the diameter of the hole in the plate to the same scale as S; d' , d'' , d''' , the diameters, to the centre of the ebonite insulation-rings, of the circular areas at H over which the measurements of the current-intensity were made for c , b , and a respectively (strictly speaking d is the mean of the diameters of the smallest and of the smallest but one areas, the corresponding curves c being the means of two sets taken with these two areas).

In the first experiments the disk D was removed, and a set of curves obtained representing the distribution of pressure and current for values of z varying from 0.20 to 1.91 centim. Of these only the curves a and c , corresponding to maximum and minimum z respectively, are given for the sake of clearness. The rest fit in satisfactorily between these two extremes, and show in every case:—

Curves I.

Curves II.

That the pressure-area increases and the pressure-intensity falls as z increases ;

That the pressure-intensity is higher for + than for - discharge, the ratio of + to - being greatest at the centre and diminishing to a value not far from unity at the edges of the pressure-area ;

That the area over which the current is received is roughly coincident with the area over which the pressure is at all considerable ;

And that the current-area is slightly greater for - than for + discharge.

A similar set of curves was also obtained with the disk D in position, the point being arranged to project about half a centimetre below the surface of D. The maximum value of z in this case was 1.88 centim. and corresponds with the curves marked *b*. As the curves for very small values of z were not materially altered by the presence of D, curves *c* may be taken to represent those for the minimum value of z in this case also.

This set of curves differs from those taken without D, mainly in the fact that they show a much smaller variation of the pressure and current areas for the same variation of z , and that the maximum pressure-intensity for + discharge is about constant, and for - discharge even increases with increase of z .

The total current passing between point and plate was kept constantly at 2.37 microamperes throughout all these experiments ; this corresponded with 80 divisions of the galvanometer-scale.

The following points may be noted in connexion with the curves :—

The pressures measured cannot depend on the momentum in the ions when they arrive at the plate, since these must strike the plate itself, and not the air in the hole H, in coming to rest. This agrees with the fact that while the pressure-curves for *b* and *c* are of the same height, the corresponding current-curves are totally unlike one another.

The pressure cannot be due either wholly or in considerable part to the imparting of momentum to the gas at the point itself ; otherwise the pressure-curves *a* and *b* would be alike, since the field at a discharging point is constant for a given current, and the values of z for both these curves are about the same.

On the other hand, the shapes of the pressure-curves are intimately connected with the shape of the field between point and plate, as is shown by the way in which the pressure-area contracts when the field is rendered parallel by D.

It follows that we must look to the dragging of the ions through the gas from point to plate for the source of most of the pressure measured on the plate; a conclusion which is consistent, so far as it goes, with the theory sketched above, and indeed suggested that theory.

Equations (iv.) and (v.) require that dP/dz should be constant. On the assumption that the lines of equal pressure are circles on the plate, centred on the point of maximum pressure, it is possible to obtain the values of P by integration from curves I. This was done, and the resulting values of P plotted with z are shown by black dots in curves III. for fifteen different values of z ; the plate D being used, and the conditions being those of curves I. If we omit the two points

for the highest value of z (see below) the constancy of dP/dz is roughly indicated. The two curves also pass very nearly through the origin so that π (equation (v.)) is small. It appears indeed to be of negative sign for the lower curve; a possible explanation of this is considered further on.

In these experiments the strength of the field was practically uniform everywhere except close to the point: its value in volts per centimetre being about 4760 for + and 3730 for - discharge. This was shown by plotting the differences of potential between plate and point with z ; the result being

two straight lines. The one for + discharge cut the axis at 1810, and that for - at 1240 volts. The only two points appreciably off the lines were those for the highest value of z . This looks as though z were wrong here, for the points fell below the lines as in the pressure-curves; and the omission of these points seems therefore reasonable.

It was possible to increase the field by arranging that the discharging point protruded a shorter distance beyond D. In this way fields of 6300 volts per centimetre for +, and 5800 for - discharge were obtained, the values of P for which are shown by crosses in curves III.

With D removed the field is of course a minimum. This was the case with curves I. a and c . Under these circumstances, however, the field was so divergent that the point would not travel far enough in its ebonite box to allow of the whole pressure being measured for values of z greater than about 0.6 centim. Only two pairs of curves were thus available in the set without D, and they are represented by the circles in curves III. Excluding the strong field close to the point, the average value of the field between point and plate in this case was 2530 volts per centimetre for + and 2300 for - discharge.

Lastly, to test the effect of variation in the current, three current strengths were used, respectively 1, 2.5, and 4 times that of the rest of the experiments. The integrated pressures for these, divided respectively by 1, 2.5, and 4, are given by the three points at $z=0.96$ centim. The highest point in each case corresponds with the lowest current, and the lowest with the highest.

All these extra points may be said to fall upon the ruled lines about as well as the majority of the original points. It is true that the coincidence is not very startling, but the discrepancies are not more pronounced for one set of conditions than another, and they are probably due chiefly to the difficulty of obtaining the correct values of the integrated pressures. It will be seen from curves I. that the pressure decreases very gradually at the edges of the pressure-area, where the pressure-intensity is also very small. The areas over which these small pressures are to be integrated become greater, however, as they are farther from the centre; and the smallness of the pressures themselves, while rendering them difficult to measure, does not therefore imply that they are negligible in the integration. In addition to this the pressures are not necessarily symmetrical about the centre line of curves I., yet the integration depends upon the assumption that they are. There is thus plenty of room for the observed irregu-

larities, and I think that curves III. afford, on the whole, considerable support to the premises of equations iv. and v.

It remains to deduce V , the velocity of the ions in unit electrostatic field.

For + discharge $dz/dP = 0.0474$ centim. per dyne.

" — " " = 0.0687 " "

$C = 2.37$ microamperes = 7100 E.S. units.

Hence

$V + = 7100 \times 0.0474 = 336$ centim. per second.

$V - = 7100 \times 0.0687 = 489$ " "

The sum of these values is 825. Rutherford's value in the same units was 960. Their ratio is 1.45. Zeleny's value was 1.25.

Experiments by the "Point and Ring" Method.

I was at first inclined to attribute the above differences to the fact that the ions studied by Rutherford and Zeleny had moved in very much weaker fields than those I used; but there is another way of accounting for them. The symbol P stands for the drag of the ions on the whole gas between point and plate. If this is all received by the plate as fluid pressure the gauge measures P ; but if there is anything like a rebound of the wind from the plate, the pressure on the plate may or may not be too great according as the momentum of the rebound is received on a fixed body or is allowed to push back the atmosphere above the plate. Now nearly all the readings were taken with the disk D in position, and it seemed possible that D had played the part of this fixed body and had thus given rise to an error of excess in the readings of the gauges. Such excess would vanish for very small as well as for very large values of z ; the pressure-curve would therefore still cut the pressure-axis at the proper point, but its slope would be too great for values of z which were small compared with the diameter of D ; and such having been the case for curves III., the values of V obtained from these curves might be expected to be too small.

By arranging that the gauge measured the difference of pressure between two opposite points on D and on the plate, the error could of course be avoided; but considering the uncertainties attending the pressure integration and the fact that each separate point in the curves represented several hours of work, it seemed desirable, if the curves were to be repeated, to improve the method. Some plan was obviously needed whereby all this labour might be replaced by a single

observation ; and after three or four unsuccessful attempts the following arrangement was hit upon.

The lettering in fig. 3 corresponds with that in fig. 2. The

discharging point B is supported in a narrow sliding glass tube, drawn out at the end B ; the plate A is replaced by a ring of smooth metal ; and the ebonite box by the wide glass tube E, of which the ends are connected to the two limbs of the U-tube pressure-gauge by the side tubes T_1 T_2 . The ring is also supported by a narrow glass tube through which passes a wire connecting it with the galvanometer, and which is itself the prolongation of a micrometer-screw. By this screw the ring can be moved along the tube, and the values of z can thus be altered and measured in terms of the screw-pitch.

If p is the difference of pressure in dynes per square centimetre measured on the gauge, and a the cross-section of E,

$$P = pa + p',$$

where P means the same as before, and p' is that part of the wind-pressure which is stopped by the ring ; it being assumed that the cross-section of E is not appreciably reduced by the presence of A and B and their supports ; and that T_1 and T_2 are so far apart that the momentum of the wind has all been converted into pressure where they occur.

This quantity p' is one of the drawbacks of the new method. It is necessarily unknown ; and it was partly in order to reduce its value to a minimum that a ring rather than wire gauze or perforated metal sheet was finally adopted to replace the original plate, A ; the idea being that the wind would pass through the ring and eddy back outside between it and the tube E without much opposition. p' can never vanish, however, unless the ring is infinitely thin, as the pressure produced by the ions just before they finish their course is

necessarily taken by the surface they are approaching. The curves for P and z are thus lowered by an unknown amount; an amount which tends moreover to increase as the ring is moved away from the point, but at a lessening rate, so that the lowering becomes constant when z is considerable. It is therefore from the higher parts only of the curves that values of V may be obtained.

In curves IV. specimens of the results obtained with the final form of this apparatus are given; each point being the mean of four observations. The straightness of the curves is unmistakable except for small values of z , where they all show the effect of the alteration of p' just referred to. Fig. 3 shows the point which is taken as the zero of z .

Curves IV.

In all, three sizes of tube were experimented with. The first, of internal diameter 1.28 centim., gave the rather low values

$$V_{+} = 342, \quad V_{-} = 423.$$

I mention these only because they appear in the Brit. Assoc. Rep. for 1898 as the best values so far obtained. It has

since been found that they are subject to two sources of error, both of which tend to lower V . Firstly, the ring was too near the wall of the tube and so impeded the return current of gas; and, secondly, the wire of the point B was uncovered for more than a centimetre along its length. That this was also responsible for some of the excess of pressure was suggested by experiments with CO_2 in which the wire became discoloured for some millimetres at its end, showing that discharge had occurred from the sides of the wire as well as from the point. Such sideways discharge would tend to creep farther back from the point as z was increased, and this would make the pressure-curve too steep. The following results of two experiments made with the same point alternately bare and covered with thin glass to within a millimetre of its end illustrate this:—

V+.	V-.	
330	406	point bare.
419	496	point sheathed.

The containing-tube, E, was of diameter 2·44 centim. in this case.

It is possible that there may have been a trace of this effect present in the experiments with the "hole in plate" apparatus; but the point was in such a strong parallel field that it could hardly have been marked.

Even with the glass sheath there was opportunity for a certain amount of side discharge as it was impossible to extend the sheath right up to the point without increasing the potential of discharge to an inconvenient extent. It was therefore important to work with large values of z so that the position of the discharge region on the point might be constant. With the two E-tubes mentioned above this was not possible as the effect of their walls on the discharge became apparent when z was increased to a couple of centimetres or less. I therefore constructed a third apparatus, of which the inner diameter of the glass tube was 6·26 centim., and the length 34 centim. With this the readings for curves IV. were taken as well as all others on which I rely. The ring (mean diam. = 2·5 centim. and thickness 0·4 centim.) was of burnished brass, and in most of the experiments there was a thin layer of vaseline on its surface to catch any dust that might be deposited by the current. All glass surfaces were carefully washed with soap

and water before use, and the air was passed through strong sulphuric acid and over phosphorus pentoxide before it entered the apparatus.

In the following table are collected all the reliable values of V obtained.

Micro-amps.	V +	V -		Micro-amps.	V +	V -	
3.2	401	516	Curve.	3.2	430	547	{ Double Position.
1.6	396	506	"	"	427	547	"
3.2	414	545	"	"	421	547	"
"	407	560	{ Double position.	"	415	514	"
"	420	513	"	"	401	534	"
"	412	524	"	"	396	524	"
"	401	547	"	"	423	520	"
"	430	526	"	3.2 }	390	629	"
"	417	515	"	1.6 }	376	620	"
"	404	510	"	3.2 }	415	540	"
"	433	602	"	1.6 }	390	551	"
"	436	562	"	3.2 }	407	539	"
"	419	557	"	1.6 }	422	541	"

Those marked "curve" are deduced from complete sets of readings such as those from which curves IV. are plotted. "Double position" means that the pressures were measured at two values of z only, situated well within the straight portion of the curve (usually at 5.18 and 3.63 centim. respectively). It will be seen that most of the determinations were by the latter method; this was for the following reason. In taking readings for a complete pressure curve I usually went up and down the range of z several times so as to get several determinations in succession of what ought to have been the same curve. These seldom coincided, however, when plotted; yet their disagreement was not haphazard, as each separate curve was usually fairly smooth, often with a gentle bend up or down indiscriminately. This could be accounted for by supposing that a small part of the pressure was variable and independent of the distance from point to ring; *i. e.* of that part of the pressure from which V is calculated. Such a variation of pressure, if it occurred gradually during the taking of the readings for a long curve, would obviously alter the slope of the curve, though there would be no corresponding alteration in V . It was therefore important to take the readings for large and small values of z alternately, and as quickly as possible; hence the "double position" method. In illustration I give the details of a complete experiment.

Positive Discharge.				Negative Discharge.			
<i>n.</i>	<i>z.</i>	P.		<i>n.</i>	<i>z.</i>	P.	
2	100	0·707	0·231	1	100	0·568	0·167
3	70	·476		4	70	·401	
6	100	·720	0·244	5	100	·568	0·179
7	70	·496		8	70	·389	
10	70	·492	0·236	9	70	·403	0·159
11	100	·728		12	100	·562	
14	70	·512	0·222	13	70	·376	0·180
15	100	·734		16	100	·556	
Mean ... 0·228				Mean ... 0·171			

n gives the order in which the readings were taken; *z* is measured in screw-threads; P in scale-divisions of the pressure-gauge; and the fourth column is the change in P corresponding to a change of *z* from 70 to 100 threads. The positive readings show well the kind of pressure-variation which may occur. It happens here to be one of increase with time, but that it has affected the pressure for both values of *z* about equally follows from the constancy of the fourth column. If the small pressures had all been taken either before or after the large ones, as they would in an ordinary curve, an error of about ± 8 per cent. would have been introduced into the resulting value of V.

It is curious how little connexion there seems to be between the variations for + and – discharge, though taken in rapid alternation. This is characteristic of most of the readings. If anything they tend to alter in opposite directions. It should be noted that these facts prove the variations to be electrical in their origin, and not, as might otherwise have been suspected, due to imperfections in the pressure-gauge, which worked smoothly and well.

Of course if the pressure-variations are not gradual the double-position method is powerless to counteract them. This is probably the reason of the somewhat large variations in the

table of results. By the same token, however, these variations will tend to be symmetrical about the true value of V , and will therefore not affect the mean of a large number of experimental results.

There still remains the question of the effect of the current-strength on V . In the light of the above it is useless to make observations on different currents at different times except in great numbers. For fair comparison the readings for two currents must be thoroughly sandwiched, and this was the case for each of the bracketed pairs in the table of results. The precaution is seen to have been justified. The average difference between the values of V for 3.2 and 1.6 microamps. respectively is 2 per cent. for + and 0.2 per cent. for - discharge only; yet the absolute values of V for the first pair of readings are the worst in the table. Whatever the disturbing cause it thus affects the pressure for both currents equally, and we may conclude that within the limits of the experiments V is unaffected by changes in the current. Above 3.2 microamps. the wimshurst refused to drive the current for sufficiently large values of z .

The following are the final mean values of V . In calculating them half weight was given to the bracketed pairs, as they required longer time for taking than the rest.

$V + = 413$ centim. per sec. in unit E.S. field.

$V - = 540$ " " " "

Their sum is thus 953, which is very close to Rutherford's value, 960. Their ratio is 1.31, which is in less satisfactory agreement with Zeleny's ratio, 1.25. There can be little doubt, however, that the ions are the same in all three cases.

Relation between Velocity of the Ions and that of the Wind.

As already pointed out, V is the velocity of the ions relatively to the electrodes; and as the air through which they move is also in motion, V is not necessarily the same as the relative motion of ions and air.

In the "hole in plate" experiments the value of the electric field was 4760 volts per centim. for + and 3730 for - discharge. The actual ionic velocities were thus 6560 centim. per second for + and 6710 for - ions, except close to the point.

From curves II. *b* the current-area on the plate is about 2.3 sq. centim. From curves III., $P +$ is about 40 and $P -$ 27 dynes. Hence if we adopt the worst possible conditions, by assuming that the drag of the ions on the air is turned completely into momentum before it reaches the plate,

and take this momentum as spread over the area 2.3 sq. centim., we have the means of obtaining an upper limit to v , the average velocity of the air.

$$\text{For } + \text{ discharge } \frac{40}{2.3} = v^2 \times \text{density of air,}$$

$$\text{or } v + = 120 \text{ centim per sec.}$$

$$\text{Similarly } v - = 95 \quad , \quad ,$$

The upper limit of v is thus only 2 per cent. of the actual velocity of the $+$ ions, and 1.4 per cent. that of the $-$ ions; and the percentage is no doubt much less in reality, as one cannot suppose that the ionic drag is all turned into momentum.

In the "point and ring" apparatus the field, and therefore the velocity of the ions, is unknown; still we may infer that v is negligible here also from the straightness of the pressure-curves; for the lines of flow of gas must be very different to those of the electricity on the average, and the motion of the gas would thus alter that of the ions in different proportions at different points in their path, if it were appreciable.

The conclusion therefore is that V is practically equal to the velocity of the ions relatively to the air they travel through.

Spread of Current between Point and Plate.

The close equality of the actual velocities of the positive and negative ions makes it a simple matter to explain the fact, noted above, that the negative ions spread more than the positive in passing from the point to the plate. For, the velocities of the ions being the same, the amount of free electricity between the point and the plate is the same for given values of z and c . But the repulsion of this electricity for itself, which is the cause of the spreading, is thus also the same for both ions if they spread equally; hence, as the negative ions move faster than the positive under a given force, they will spread farther.

By altering the strength of the field we affect the spread in two ways. If the field is increased the time taken by an ion to pass from point to plate is decreased in proportion. Also the quantity of electricity between point and plate, *i. e.* the spreading force, is decreased in the same proportion. On these lines it is easy to show that if the spread is not too great, and if c and z are both constant, $V \propto 1/F^2$ for constant spread. This suggests a simple method of comparing the values of V for different physical conditions of the gas.

Mass of the Ions.

Equation (v.) contains the symbol π , which stands for that part of the pressure resulting from the momentum of the ions themselves. If F represents the strong field close to the point in which the ions start, e the ratio of the mass of the ion to the charge it carries, and C the current from the point,

$$k\pi = CeVF,$$

where k is 1 if the ions all start in the direction in which the pressure is measured, 2 if they radiate uniformly along the normals to the hemispherical surface of the point, and greater than 2 if any of the discharge takes place from the sides of the point. For a weak current, or for a point in a strong parallel field, k will thus lie between 1 and 2.

The positive curve in curves III. cuts the line of dynes above the origin. Calculating the position of the cutting point from the seven lowest readings gives $\pi = 0.76$ dyne; or, by taking all the readings except the highest, $\pi = 0.66$ dyne. k is unknown; say 1.5. $C = 7100$ E.S. units. $V = 413$. F for a point of diameter 0.0055 centim. = 1870 E.S. units*, hence

$$e = \frac{1.5 \times 0.7}{7100 \times 413 \times 1870} = 1.9 \times 10^{-10} \text{ E.S. units.}$$

For oxygen the electrolytic value of e is 2.8×10^{-14} E.S. units. On Rutherford's hypothesis of molecular clusters this would mean that the diameter of each cluster contains $\sqrt[3]{1.9 \times 10^{-10} \div 2.8 \times 10^{-14}} = 19$ ordinary molecules in a row. Rutherford himself estimates the number at 5.5 for air; his calculation being based on considerations of viscosity. His result, however, really means that the diameter of the sphere of action of a molecular cluster is 5.5 times that of a single molecule of air, which is not necessarily the same thing. For it seems unlikely that the molecules forming a cluster do not come nearer than just to feel each other's influence; and if they do, there must be more than 5.5 in the diameter. The two results are therefore not inconsistent.

With the ring and point apparatus so far employed π was not obtainable. I therefore took a larger and thinner ring of

* This is calculated from a formula which I found for the field at a point just on the verge of discharging, as I have since satisfied myself that this field remains nearly constant while the discharge is occurring. The proof of this I hope to publish shortly in connexion with other work. The formula is $F = 16.5 \times r^{-0.8}$, where r is the radius of the point in centimetres, F the field close to the point, and air the gas; the discharge being positive. For negative discharge divide by 1.3. (Phil. Mag. Sept. 1891, p. 293.)

wire (diam. 4.7 cm., thickness 0.07 cm.) and placed the point at its centre (fig. 4). If under these conditions the electricity were to arrive at the ring equally on both sides, the pressure measured on the gauge would be π . It would, however, certainly travel most to the side remote from the point, as indicated by the dotted lines, and the pressure would thus be too large; but by repeating the measurements with a point of, say, larger diameter, at which the discharging-field would therefore be less, the difference between the pressure-readings should give the change in π due to the change in field.

Points of diameters 0.0066 cm. and 0.0306 cm. respectively were used for this purpose; their respective discharge-fields for positive electricity being 1600 and 640, and for negative 1230 and 490 E.S. units. It was necessary to take a large number of readings as the pressure-variations mentioned above were of course again met with, and, the pressures themselves being extremely small, these variations were rather serious. Thirty-five observations with an average current of 7930 E.S. units gave mean pressures of 3.9 dynes with the thin point and 3.3 with the thick for positive discharge; the corresponding pressures for negative discharge being 2.65 and 1.50 respectively. Substituting in the above equation for e the values 3.9–3.3 for π , 1600–640 for F , and 7930 for C , we obtain 22 as the number of molecules in the diameter of a positive cluster. For the negative cluster the number is 27, using the values of π and F for negative discharge. 22 agrees well with the previous 19; a good deal better, in fact, than the many sources of error would lead one to expect; but the number for the negative clusters is likely to be too large, as the negative discharge from the blunt point formed a luminous projection which stood out from it farther than that from the sharp point. If this represented a line of dissociated gas it would behave like a conductor, and the pressure-producing part of the discharge would thus be starting from the outer end of it. This would make the pressure too low; and the change in pressure, on changing from blunt to sharp point, too high.

It is a pity that there is no check to be had to this from the negative curve in curves III., which appears to give a negative and therefore impossible value to π . The probable reason for this is, however, an interesting one on its own account. About two years ago, in measuring the field in air at a sharp discharging-point, I found that, in the case of positive discharge, the field was almost constant for the widest range of current I was able to apply when discharging onto a smooth cathode of large area; but that if even a small amount

of current passed the other way, as occurred when the cathode was provided with a sharp point projecting slightly from its surface, the field at the original (anode) discharging-point might be lowered 20 or 30 per cent. or more. With the electrification reversed, on the other hand, this was not the case to anything like the same extent.

Negative ions arriving at an anode thus greatly facilitate discharge at the anode; while positive ions arriving at a cathode produce very little effect. I am therefore inclined to attribute the negative value of π in curves III. to a small back-discharge from plate to point brought about by the negative ions arriving at the plate.

Miss W. E. Walker, who is at present engaged in applying the "point and ring" method to non-conducting liquids, finds very marked indications of a similar back-discharge in certain liquids; and, with them as with air, most particularly for negative ions arriving at a positive ring. The same sort of effect has also been met with in vacuum-tube experiments. The whole question of back-discharge is very interesting, as being likely to throw light on the mechanism of discharge; and I hope soon to publish an account of the facts upon which the above statements are based.

In the experiments with the thin ring the back-discharge, if it occurred, would increase instead of decreasing the pressure, as its direction would, on the average, be that of the arrows, *b* (fig. 4), which obviously act the same way as the

Fig. 4.

arrows, *a*, of the direct discharge from the point. Error would therefore still be introduced into the value of π , unless *b* happened to be constant for both the points. Here, again, there seems to be reason for doubting the accuracy of the number for the negative cluster.

A last source of error, common to both positive and nega-

tive discharge, is the fact that k is probably less for blunt than for sharp points with a given current.

The smaller the current, however, the smaller this discrepancy will be; and a small current is also likely to give rise to a smaller back-discharge error. On the other hand, the error which is due to the luminous projection from the negative point may be reduced by using a sharper point. Two points of respective diameters 0.013 cm. and (approx.) 0.001 cm. were therefore selected, and sixty observations of the π -pressure made as before with each for an average current of 990 E.S. units. Taking $k=1.5$ the number of molecules in the diameter of a positive cluster deduced from these data was 16; that for the negative cluster 12. These numbers are consistent with the higher speed of the negative ions, besides being likely to be more reliable than those given above for the reasons just stated. Whether the use of still smaller points and currents, if it were practicable, would alter them much it is impossible to say. At least they represent the order of magnitude of the quantities concerned, and they thus afford considerable support to the theory of molecular clusters.

In conclusion I wish to express my thanks to Mr. E. H. Dixon for valuable aid during the later experiments on the estimation of π ; and to my assistant, Mr. Herbert Strachan, who helped me with the greater part of the work, and to whose skill and patience much of the success of the experiments is due.

*XLV. Description of a New Spectrophotometer and an Optical Method of Calibration. By Prof. D. B. BRACE, Ph.D.**

TO Govi, Vierordt, Crova, Cornu, Glazebrook, Wild, König, and Lummer and Brodhun, and others are due different types of spectrophotometric instruments. The arrangement adopted by Govi, Vierordt, Crova, and others of bringing the two spectra to be compared into contiguous positions by means of double slits and total-reflecting prisms fails in eliminating the dark line separating the two, and thus reduces the sensibility of the eye in determining a match, as is well known to be the case unless the bounding lines of the two fields are perfectly sharp, and vanish completely when set for a match. The same defect exists in the polarizing arrangements of Glan, Crova, Glazebrook, König, and others, where the two spectra are brought into juxtaposition by

* Communicated by the Author.