EVIDENCE FOR THE EXISTENCE OF HOMOGENEOUS GROUPS OF LARGE IONS.

By P. J. Nolan.

Synopsis.

Homogeneous groups of large ions in air.—The existence of such groups, which seemed proved by previous work reported by the author and others, has recently been questioned by the negative results obtained by Blackwood. Hence further experiments have been made using the Zeleny method adopted by Blackwood instead of the McClelland method previously employed. The thirty curves obtained nearly all show two or more peaks or breaks corresponding to definite groups. These peaks came at the same places whether the ions were produced by bubbling the air through alcohol or by passing it over phosphorus. *The mobilities of the groups* agree with the values previously reported within 10 per cent. or less: .050, .025, .018, .0075, .0042, .0025, .0013, .00067, .00033. Some evidence of intermediate groups was also obtained. *In explanation of Blackwood's negative results* it is suggested that since ions are constantly changing from group to group, definite peaks can be expected only if the time spent by each ion in the measuring chamber is relatively short. In Blackwood's experiments this time was from 9 to 150 seconds whereas it was only from 0.5 to 13 seconds in the experiment reported here.

In various papers[1] published between the years 1916 and 1919 the present writer and others have described experiments showing that, when large ions are produced in air in various ways, the ions can be divided into a number of groups, each group having a definite mobility. In a paper[2] recently published Blackwood presents evidence against the existence of such groups. He finds that the ions distribute themselves continuously over a wide range; in other words he finds "a continuous spectrum of mobilities and not a band spectrum." The present paper gives the results of a reëxamination of the question in the light of Blackwood's criticisms. The evidence here presented is, it is felt, quite convincing as to the existence of the group system and is on the whole a very complete confirmation of previous work.

A short account of the work on group ionization will show that the conclusion that this type of ionization exists was not rashly made. The first indication of groups was obtained in 1912 by J. J. Nolan while working at the electrification caused by spraying water and mention is made of the groups in a paper[3] published in 1914. Before the examina-

[1] J. J. Nolan, Proc. Roy. Irish Acad., Vol. 33, (A), 1916. J. A. McClelland and P. J. Nolan, Proc. Roy. Irish Acad., Vol. 33 (A), p. 24, 1916; Vol. 34 (A), p. 51, 1918; Vol. 35 (A), p. 1, 1919.

[2] Blackwood, Phys. Rev., Aug., 1920.

[3] J. J. Nolan, Proc. Roy. Soc. (A), Vol. 90, 1914.

tion of these groups was completed J. A. McClelland and P. J. Nolan discovered groups in the ionization produced by bubbling air through mercury. When the mobilities were calculated and compared it was found that there was a considerable amount of numerical agreement between the values for the mobilities of various groups. The method of measuring mobilities used was the well-known McClelland method in which the ionized air is drawn along a tube containing an insulated central electrode and curves are plotted between the voltage on the outer tube and the currents to the central electrode. These curves were found to consist of a number of straight lines indicating the presence of distinct groups of ions. The mobilities of the groups were deduced by taking the voltages corresponding to the corners as the saturation voltages for the different groups. The obvious objections to the McClelland method as a method for separating out possible groups of ions of mobilities not widely different were fully realized, but careful consideration failed to account for the experimental results on any other hypothesis than that of the existence of separate groups. Experiments conducted with different methods of producing the air-blast through the mobility tube and also with mobility tubes of different dimensions confirmed the existence of groups. The results on the spray ions and on the ions due to mercury were published at the same time with a joint discussion.

Table I., column A, gives the mobilities of the ions obtained with water and columns B to E give the mobilities observed with mercury with dried and undried air and with long and short time-intervals between production and measurement. It was thought that the mobilities given in columns C, D and E represented groups which were gradually growing and that the final stable sizes were the ions given in columns A and B. The coincidence between the numbers in columns B and D, C and E which are set forth in the table were at the time thought to be accidental. The spray ions did not show any change with time. It was supposed that the ions from mercury took time to add on water vapor, the approach to stable conditions being delayed, in the case of the experiments with partially dried air, by the diminution of the amount of water vapor present.

Further work on the ionization produced by bubbling air through alcohol and by passing air over phosphorus revealed the presence of groups of ions in both cases. In the determination of the mobilities of the various groups the following method was adopted. A preliminary investigation of the current-voltage curve was made and a portion which contained only one corner was selected. This portion was explored very carefully to ensure that it was made up of two intersecting straight lines

TABLE I.

Water.	Mercury.				Alcohol.	Phosphorus.
	Long Time-Interval.		Short Time-Interval.			
	Undried.	Dried.	Undried.	Dried.		
A	B	C	D	E	F	G
1.09					1.10 ?	
.53					.50	
				.32	.31	
.24			.20		.22	.22
.12					.12	
				.092		.092
.046			.048	.043	.049	.053
		.024				.028
.013	.014		.02		.017	.018
		.0068		.0064	.0077	.0074
.0043	.0040		.0045		.0040	.0041
		.0021		.0022	.0023	.0024
.0010	.0013		.0013		.0014	.0012
		.00056			.00063	.00064
.00038	.00034				.00034	.00031
					.00015	.00015
						.000085
						.000053

and to determine the exact point of intersection. In all about 250 such curves were plotted during the course of the alcohol and phosphorus experiments. Table I., column F, gives the mobilities of the ions found in air which had bubbled through alcohol. The results with alcohol caused a modification of the views previously advanced. With alcohol both the series of groups due to water and due to mercury under dry conditions were obtained and no gradual change with time in the mobility of any group was observed in spite of the fact that a large number of observations was taken at a wide range of time-intervals and in the critical manner just described. The agreement of the mobility values as illustrated in Table I. was striking. We were thus driven to the conclusion that each group represented an ion of at least some degree of stability. The fact that the opposite result was expected when the work was undertaken gives all the more value to the conclusion arrived at. The results of the phosphorus investigation are given in column G; the groups given there were observed when dried air as well as undried air was passed over phosphorus. The phosphorus observations supported the previous conclusion that the mobilities were definite and did not change with time. The agreement between the mobility values gave still further confirmation of the group idea.

APPARATUS AND METHOD.

The work described in the present paper was commenced as soon as possible after the appearance of Blackwood's paper. As he had based his conclusion that there were no groups on results obtained with the Zeleny method, it was decided to use that method in trying to confirm our previous work. Blackwood examined the ionization produced by spraying water and also that formed when air is passed over a hot platinum wire. The writer has never investigated the ionization produced in the latter way but the experience of other workers in this laboratory is that it is difficult unless very special precautions are taken to obtain steady conditions when dealing with this type of ionization. The quantity of ionization obtained by bubbling air through alcohol or by passing air over phosphorus is much larger than that due to spraying water. Another important consideration is that in the water spraying experiments of J. J. Nolan, the results are not consistent in the region of the larger ions.[1] Variations are observed in the mobility values of two of the groups which are larger than would be expected from experimental errors. Two observations of a mobility which does not enter into the group system are recorded. Variations in the quantities of the different groups are noticed. This variation is especially noted in the largest ion and sometimes the quantity of this ion present is so small that it would be difficult to assert that it was not absent. These considerations led to the use of the alcohol and phosphorus methods of producing ionization in preference to the hot wire and water spray methods. This decision was also influenced by the fact that the writer is more familiar with the former methods.

The arrangements of the apparatus for bubbling air through alcohol and for passing air over phosphorus were essentially the same as those described in previous papers. The Zeleny method of measuring mobilities, as used by Blackwood, consists in drawing the ionized air through a tube containing two central electrodes separated by a short gap. The longer electrode is earthed and the shorter electrode, which is the farther from the entrance to the tube, is insulated and connected to an electrometer. Curves are drawn with the voltages on the outer tube as abscissæ and the currents to the short insulated terminal as ordinates. It is easy to show that if there are present ions of one mobility the curve will consist of one peak and that if several groups of ions are present there will be several peaks, one corresponding to each group.

Two Zeleny mobilities tubes were used during the course of the work; their dimensions are as follows:

[1] P. R. I. A., Vol. 33 (A), p. 17, 1916. P. R. S., Vol. 94, p. 126, 1917.

Internal diameter of outer tube (in both tubes)	= 3 cm.
External diameter of inner electrode (in both tubes)	= .95 cm.
Length of earthed electrode	37.4 and 10 cm.
L_1 length of insulated electrode	12.3 and 5 cm.
L length of earthed electrode + insulated electrode + gap	49.8 and 15.1 cm.

One tube was more than three times as long as the other and the ratio L/L_1 was approximately four in the long tube and three in the short tube. The tube which Blackwood used was nearly three times as long as the longer tube and his ratio L/L_1 was four. This ratio is important because the bigger it is the more pronounced should be the peaks on the Zeleny curve. On the other hand, the larger the ratio the smaller will be the quantity of ionization for measurement. The shortening of the insulated electrode introduces another very serious difficulty, the nature of which will be referred to later.

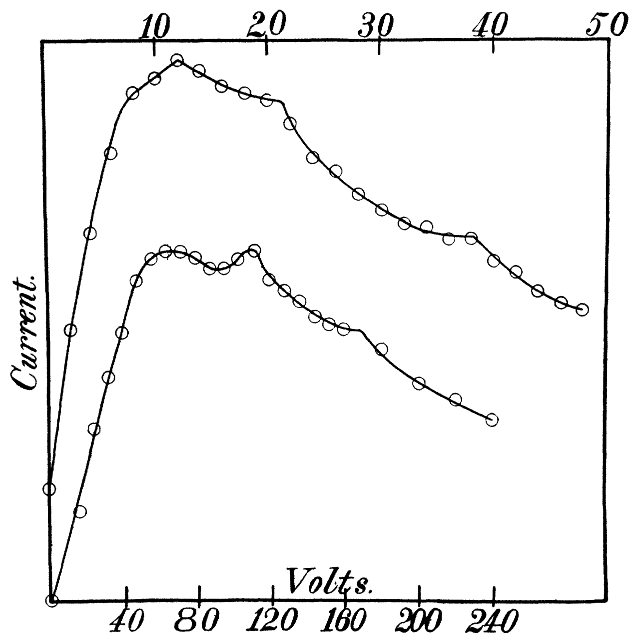

Fig. 1.

Results with Alcohol.

The ionization produced by bubbling air through alcohol was first tested using the long mobility tube. One of the first curves obtained is the upper curve given in Fig. 1. The voltages referring to this curve are shown along the upper horizontal line of the figure. In general outline it resembles the curves given by Blackwood. There is only one peak but there are two decided corners at 21 and 38 volts and perhaps a corner at 7 volts. If voltage steps twice as large had been used these corners would scarcely have been detected and a smooth curve would have been the result. Although these corners show clearly that there is not a continuous spectrum of mobilities, there is a wide difference between this curve and the theoretical curve given by Blackwood, the realization of which experimentally he looked for as a confirmation of the existence of groups. This theoretical curve is that due to three groups of ions of mobilities in the ratio 1, 2.5 and 11 present in equal quantities and it shows three well-defined peaks. Our experience shows that the groups are present in varying proportions which seldom approach equality. If a theoretical curve were drawn with one group present in large quantity and others in smaller quantities, the peaks would not be so well marked. Again with alcohol and phosphorus the ratio of mobilities is 1, 1.8, 3.4, etc. The ratio of successive mobilities has a considerable influence on the appearance of the Zeleny curve; the closer the mobilities the less defined are the peaks. We have given reasons why the spray ionization was not used and we considered that these reasons outweighed the advantage that the spray ions are in general more widely spaced than the ions due to alcohol or phosphorus. Making allowance for the inequality in the amounts of the different groups and the closeness of successive mobilities a theoretical curve would be drawn with peaks not so well marked as in Blackwood's theoretical curve. These two considerations, however, are not sufficient in themselves to explain the non-appearance of peaks in this curve. An explanation may be found by consideration of the fact that the ions are changing while passing along the mobility tube. This will cause a rounding-off of the peaks and a filling-up of the hollows in the theoretical curve as ions which grow during their passage through the tube will appear to have mobilities which are between their initial and final values in the tube. It is obvious that if a very long mobility tube and a very slow air-blast were used the ions would spend a long time in the tube and the effect of change might be so great as to obliterate any evidence whatsoever of groups. Accordingly we can interpret the corners on the curve as peaks of the theoretical curve which are flattened and almost obscured by the growth of the ions in the tube. If this interpretation is correct the curve indicates the presence of three groups (and a possible fourth) the mobilities of which can be deduced by taking the voltages at the points of discontinuity as saturation voltages for the various groups. Furthermore it should be possible to obtain curves more like the theoretical curve by reducing the time which the ions spend in passing along the mobility tube. Experiments were accordingly conducted with various air blasts faster than that used in the first experiments. Various volumes of tubing were inserted between the bubbling vessel and the mobility tube so that the time interval between the formation of the ions and the measurement of their mobilities might be equal to or in some cases greater than the time-interval used in the previous experiments. The longer this time-interval, the bigger will be the ions when they reach the tube and consequently the less will the ions change when passing along the tube. The time of the ions in the field can also be reduced by reducing the length of the tube and it was with this object that the shorter mobility tube was used in some experiments.

The lower curve in Fig. 1 was obtained using a faster blast than that used in the previous experiments. This curve shows two well marked humps and one corner. This curve is more like the theoretical curve; one peak is like the peaks in the theoretical curve but the other peak is much flatter. This curve places the existence of group of ions beyond any doubt. The two peaks are undoubtedly due to two distinct groups of ions and the corner indicates the presence of a third group.

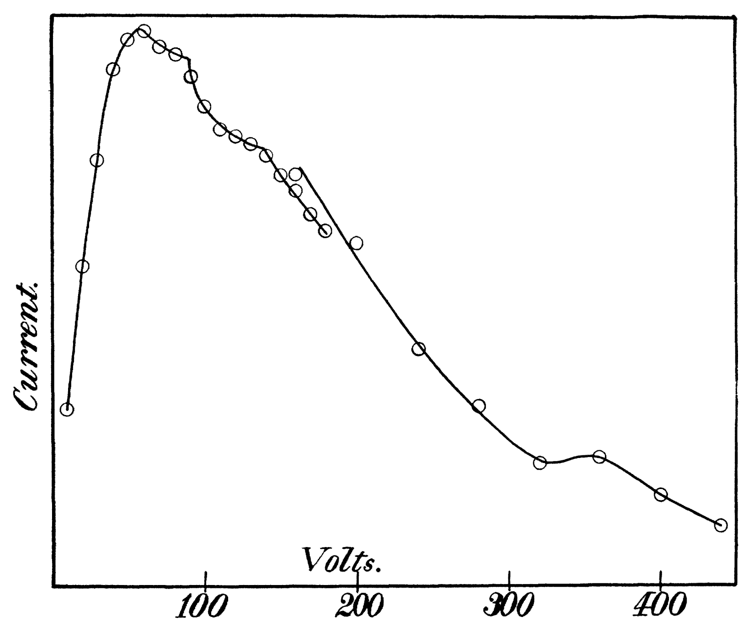

Fig. 2.

Fig. 2 gives another sample of the curves obtained with the alcohol ionization. Two parts are shown representing separate experiments in which the conditions were the same. In this curve there is a peak, two corners and a hump at a high voltage. The hump at 360 volts is convincing evidence of the existence of a separate group of mobility approximately equal to .00067 cm./sec. A preliminary consideration of the theoretical Zeleny curve, taking into account the various causes which might obscure peaks, led to the conclusion that peaks would be more easily observed on the right hand side of the maximum point of the curve. This conclusion was justified by the results obtained during the course of the work.

To obtain still better definition of the peaks experiments were performed with faster blasts and with the shorter mobility tube. Results so obtained will be discussed later.

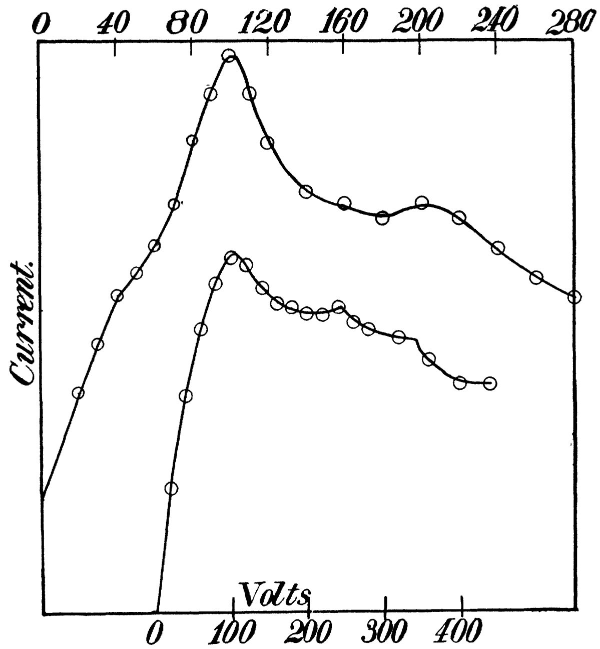

Fig. 3.

Results with Phosphorus.

The upper curve in Fig. 3 is due to the phosphorus ionization, the longer mobility tube being used. There are two well-marked peaks and one corner, showing clearly that groups exist in air passed over phosphorus. The lower curve in Fig. 3 gives another sample of the phosphorus curves; it shows the presence of three groups. Curve *A*, Fig. 4, is the only instance of a definite peak at a small voltage well removed from the maximum peak of the curve. It is plotted with the means of two series taken, one immediately after the other, which agreed very well. When

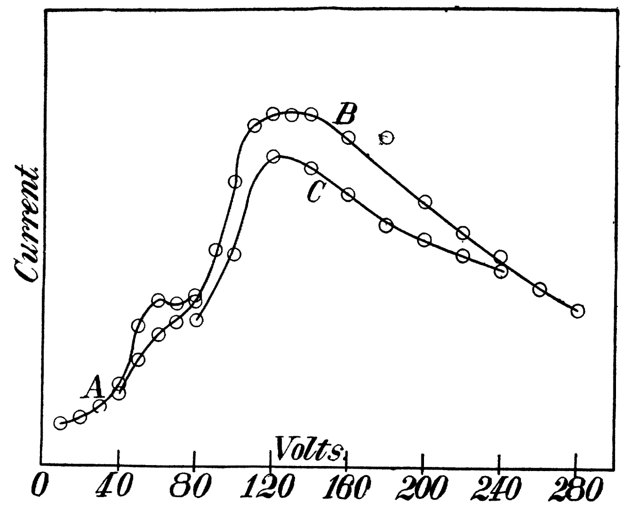
B
C
A
Current.
Volts.
0
40
80
120
160
200
240
280

Fig. 4.

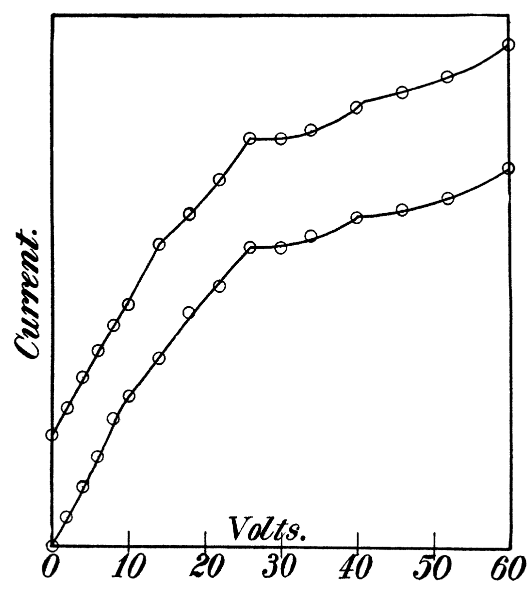
Current.
Volts.
0
10
20
30
40
50
60

Fig. 5.

the complete curve B was taken this peak at 60 volts had become flattened out but there still remained evidence of a group at this point. Curve C taken immediately after Curve B gives the same mobility for its highest point but its peak is sharper. It is an interesting fact that the sharpness of the peaks varies considerably and in this case the variation occurs during an immediate repetition of the numbers. In the previous paper on phosphorus changes in the nature of the ionization were recorded and also the fact that some of the groups of ions could not be observed on some occasions. The three curves in Fig. 4 also show a variation in the quantity of the ionization. This variation was often noticed when observations were repeated both in the case of the phosphorus and alcohol but it is thought that such variations do not affect the validity of the arguments from the whole series of curves. It may be noticed that the number for 180 volts in curve B is well above the curve. A peak is not drawn here because it would depend on only one number and it does not appear in curve C. The peaks and corners on which we rely depend on current observations for several successive voltages and are supported by other curves. A slight continuous variation of the quantity of ionization during an experiment such as sometimes occurred does not affect the general evidence of the curves. It may be remarked here that in the previous work by the McClelland method practically all the curves were drawn using the means of observations with ascending and descending voltages. As in those experiments a short part of the curve was examined, the experiment was performed in a short time and the variations which occurred during a series of observations were small.

Fig. 5 gives portion of a curve worked over in detail using the smaller mobility tube. One curve was taken immediately after the other. The difference between the two sets of numbers is very small. The curves are plotted apart with different zeros but as the zero for both curves is given it will be seen how good is the agreement between the readings for the various voltages. There is a well marked corner at 26 volts and a faint corner about 40 volts in both cases. It is interesting that the corner at 26 volts is so well marked as the mobility deduced from it (.033) cannot be fitted into the groups we have already found. There is some evidence of corners about 8 volts in one curve and about 14 volts in the other curve. However as this region was not fully explored there is no further evidence for or against groups at these points. A slight difference in the numbers about this region in the two curves causes the appearance of the corner at 8 volts in the one case and at 14 volts in the other. This lack of agreement also prevents us from making any decision.

This completes a selection of the curves obtained. In all about thirty curves were taken and only two of these curves showed no evidence of a peak or corner in addition to the main peak. The failure to obtain evidence of groups on these two occasions can be explained. One of these curves was taken with a slow blast and this as we have seen militates against the observation of groups. In the other curve only two numbers were taken on the left hand side of the maximum point of the curve and possibly a corner there escaped notice.

Intermediate Mobilities.

During the course of the alcohol investigations an attempt was made to get if possible even better defined peaks by shortening the time of the ions in the mobility tube. Fast air-blasts were used and the shorter mobility tube was also used with this object. The curves obtained did not show better defined peaks but they indicated the presence of some groups of intermediate mobilities. The mobilities calculated from the previous experiments agreed fairly well with the numbers set forth in Table I. The curves now obtained showed not only these mobilities but indicated that some groups of mobilities of intermediate values were present. This matter was not fully investigated and all that can be said at present is that indications of such intermediate groups were noticed. These groups may merely represent stages in the process of growth of the ions or in other words less stable aggregations which persist for a short time in the growth between two more stable ions. The percentage of such ions present will be smaller than the percentage of the more stable ions and consequently a good resolving method is necessary for their discovery. This agrees with the fact that indications of their presence were obtained when using the Zeleny method in the manner in which one might expect the best definition of peaks. The presence of such groups would explain why the main peaks were not better defined in previous experiments and might also account for the variation in the width of the peaks.

Agreement with Previous Results.

The general agreement between the mobility values obtained by the Zeleny method and those obtained by the McClelland method is shown in Table II. The present numbers are not so numerous or exhaustive as the previous ones. Mobilities of intermediate groups are not included.

TABLE II.

Al. (McC.)	.049		.017	.0077	.0040	.0023	.0014	.00063	.00034
Ph. (McC.)	.053	.028	.018	.0074	.0041	.0024	.0012	.00064	.00031
Al. (Ze.)	.049	.025	.018	.0075	.0045	.0026	.0014	.00067	
Ph. (Ze.)		.022		.0075	.0043	.0026	.0014	.00074	.00035

BLACKWOOD'S RESULTS.

It is possible to explain fairly satisfactorily the difference between the results obtained by the writer with the Zeleny apparatus and Blackwood's results with the same type of apparatus. We have already emphasized the importance of the length of time spent by the ions in the mobility tube and it is interesting to compare the researches in this respect. If we divide the volume of the tube by the volume of the blast per second we get the average time of the ions in the tube. The volume of the tube $= \pi(b^2 - a^2)L$, where b is the internal diameter of the outside tube, a is the external diameter of the electrode and L is the sum of the lengths of the earthed and insulated terminals and the small gap between them. In Blackwood's apparatus $L = 140$ cm. and the cross-section $= 16.5$ sq. cm.; in the author's apparatus $L = 49.8$ cm. and the cross-section $= 6.4$ sq. cm. The corresponding volumes are 2310 c.c. and 320 c.c. approx. Thus for the same air-blast the time of the ions in the tube was seven times longer in Blackwood's experiments than in ours.

From the summary of Blackwood's paper published in the Proceedings of the Nat. Acad. of Sciences, May, 1920, we see that in the experiment there quoted the ions of mobility .0004 cm. per sec. would be saturated at about 40 volts. This enables us to calculate the air-blast and we thus deduce that in this experiment the ions spent about 150 seconds in the mobility tube. Similarly from the curves given in Fig. 11 of Blackwood's paper in the PHYSICAL REVIEW it can be calculated that the corresponding time in the experiments with the hot wire was about 9 seconds. These experiments were conducted for the purpose of examining the relation between the mobility and the age of the ions and were apparently carried out with the fastest air-blast used. Thus it seems probable that the extreme values of the time of the ions in the tube were 150 and 9 seconds. In our work the extreme values for this time were 13 and .5 second. The times in our experiments were much shorter than Blackwood's and we think that this to a large extent explains why he failed to detect groups. It is possible that if he used smaller voltage-steps, especially in the experiments conducted with fast air-blasts, some discontinuities might have been observed. If intermediate groups are present even in small quantities they would have an obscuring effect on the peaks of the

Zeleny curve. Possibly this is a contributory cause of Blackwood's failure.

In examining spray ions by the McClelland method, Blackwood obtained curves showing breaks, indicating a ratio of about 2 for successive mobilities. Table I. shows that J. J. Nolan found the spray ions had a ratio of about 3.4 between successive mobilities. The ratio in the case of the phosphorus and alcohol ions is about 1.8. It is possible that in Blackwood's experiments the ions of mobilities such as .00064, .0023, .0075, etc., were present just as in the case of alcohol and phosphorus. (J. J. Nolan observed the group of mobility .00064 sometimes.) This would account for the ratio observed. We have never properly understood why there should be twice as many groups in ionization due to alcohol or phosphorus as in that due to water or mercury. It may be connected with the relative quantities of positive and negative ions. In the case of alcohol and phosphorus the number of ions of the two signs are always exactly equal; with water and mercury this is not so.

McClelland Method.

It is interesting in the light of the new information about the growth of the ions and the possible existence of intermediate groups to discuss the previous results obtained with the McClelland method. Blackwood shows that the Zeleny method is much better than the McClelland as a detector and resolver of group ionization. The question then arises as to how the groups were obtained with the McClelland method and not with the Zeleny method as used by Blackwood. Comparison of the length of the time which the ions spent in the tube explains this to some extent; in previous work with the McClelland method that time-interval was generally of the same order as that used in the present work and was thus smaller than the time in Blackwood's experiments. But there is another important consideration which shows that the flattening out of the theoretical curve due to the growth of the ions is much more serious in the Zeleny method than in the McClelland method. The ions captured in the insulated terminal of the Zeleny tube are those which have moved along the greater part of the tube; in the McClelland method ions begin to be captured on the insulated terminal at the moment of their entry into the field. Hence the effect of change of the ions is smaller in the McClelland than in the Zeleny tube; the larger the ratio between the earthed and the insulated electrodes of the Zeleny tube, the greater will be the effect of growth.

If intermediate groups exist it is not surprising that they were not detected by the McClelland method. They are probably present in small quantities and the McClelland method was not able to resolve them from groups nearly equal in mobility present in large quantities. It was only when the Zeleny method was being used in a highly resolving manner that indications of these intermediate groups were noticed.

CONCLUSION.

The results obtained in the present work place beyond doubt the existence of homogeneous groups of large ions. The curves admit of no other explanation. The numerical agreement between the mobility values of the different groups deduced from the Zeleny curves and from the McClelland curves shows that both types of curves have been correctly interpreted. The present paper suggests the reasons for Blackwood's failure to find any evidence of groups. Furthermore, it shows how it was possible to detect and examine groups of ions in the previous work although it was carried out by a method of admittedly inferior resolving power.

The results of the present paper do not enable us to add to the hypothesis put forward by J. J. Nolan to account for the production of different classes of ions. It seems likely that further knowledge of the nature of this ionization will be obtained more readily by attacking the question from a different angle rather than by continuing work on the present lines.

The author wishes to express his indebtedness to his brother, Professor J. J. Nolan, for his help and advice during the course of this research.

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March, 1921.