

THE CONSTITUTION OF GASEOUS IONS

BY J. J. NOLAN

ABSTRACT

Mobilities of various groups of ions in dry and moist air.—Using the Franck modification of the Rutherford alternating current method, with the plate and gauze accurately parallel and 2.5 cm apart, current-voltage curves were obtained as the 52 cycle voltage was increased from 200 to 500 volts. Previous experiments have shown the presence of four predominating types of positive ions with mobilities of 2.04, 1.73, 1.52 and 1.34. The curves now reproduced show periodic inflections about every 10 volts which indicate intervening groups making some twenty groups of ions with mobilities varying from 2.24 to 1.34. These values agree closely with those computed according to *J. J. Thomson's theory for clusters* of from 15 to 36 water-molecules. In dry air the groups with the lower mobilities are less prominent. Other experimental evidence is cited in favor of the cluster theory as opposed to the small ion theory of ions. Loeb's criticism of the author's work is discussed and it is shown that there is no real divergence between these results and those of Loeb.

THE constitution of the ions in gases at normal pressures is still a matter of controversy. In various papers^{1,2,3} the present writer has brought forward evidence which, if accepted, would be decisive in favor of the older cluster theory as against the more recent view which regards the gaseous ions as simply charged molecules. It was claimed that these experiments demonstrate that the normal ionization consists of a mixture of distinct groups having mobilities not widely different from one another, and that in addition there are present in small numbers groups of ions of much higher mobility. These conclusions have been contested by Loeb⁴ who holds that his experiments demonstrate the existence of only one type of ion. He is of opinion that results which suggest a complex ionization are spurious and are due to "failure to observe some of the fundamental conditions" of successful experiment. The object of the present paper is, firstly to describe fully the apparatus and the experimental method used by the author so as to permit of criticism on that head being definite; secondly to show that the results of Loeb when properly interpreted, not merely do not controvert but actually support

¹ J. J. Nolan, Proc. Roy. Irish Acad. **35**, 38 (1920)

² J. J. Nolan, Proc. Roy. Irish Acad. **36**, 74 (1923)

³ J. J. Nolan and J. T. Harris, Proc. Roy. Irish Acad. **36**, 31 (1922)

⁴ L. B. Loeb, Journal Franklin Inst. **196**, 537 (1923)

the contentions of the present writer; and finally to bring forward further evidence as to the structure of ions in air.

APPARATUS AND EXPERIMENTAL METHODS

The method of measuring ionic mobilities employed in the work under discussion is the well-known modification of Rutherford's method due to Franck. Ions are produced on one side of a metallic gauze and those of one sign are driven by a steady field through the gauze. Here they come under the influence of an alternating field of sine form between the gauze and a parallel plate. If the potential difference is such that its value read on an electrostatic voltmeter is greater than $\pi nd^2/\sqrt{2}u$ where n is the frequency, d the distance between the gauze and plate and u the mobility of the ions, some of the ions coming from the gauze will be captured by the plate before the reversal of the field. For fields less than this value the plate will receive no charge. If the current to the plate is plotted against the voltage and if there is only one kind of ion present, a smooth curve should be obtained. This curve should intersect the voltage axis sharply at the critical voltage, and from the value of this the mobility of the ion can be readily determined. If there is more than one kind of ion present, the slope of the curve will increase sharply at the critical voltage peculiar to each type of ion.

As the apparatus employed has varied somewhat from time to time, it is proposed to describe the particular form with which the results given later in this paper were obtained. The modifications adopted in other work will then be indicated. The essentials are shown in Fig. 1.

The plate which receives the ions was mounted as follows. A thick brass plate, 13 cm in diameter was securely screwed on to an ebonite plate of the same size and 1.3 cm thick. The face of the plate was then turned flat in the lathe and a circular cut less than 1 mm in width was made separating an inner circular plate 8 cm in diameter from a guard-ring, which was thus a little less than 2.5 cm wide. The plate system was supported by a stout brass rod passing through an ebonite plug in the iron plate which formed the base of the apparatus. This rod served as a connection between the insulated plate and the electrometer. The guard-ring was connected to the iron plate and thus to earth. The gauze, 8 cm in diameter, was fitted to a brass ring of the same dimensions as the guard-ring. The gauze was made of brass wire .35mm in diameter and had approximately 50 meshes per cm². Great care was taken in soldering the gauze to the brass ring to make it quite taut so that no sagging could occur. It was necessary to insure that the lower surface of the gauze was flush with the ring. A flat circular plate was prepared slightly less than

8 cm in diameter and of a thickness equal to the difference between the thickness of the ring and of the gauze. This plate was placed against the gauze on the upper side and the whole clamped firmly in a vise over night. In consequence of these precautions, the under surface of the gauze was quite level, and its distance from the plate was given very accurately by the height of the three ebonite pillars supporting its rim. The pillars were carefully turned in the lathe. Their diameter was 1.1 cm and their

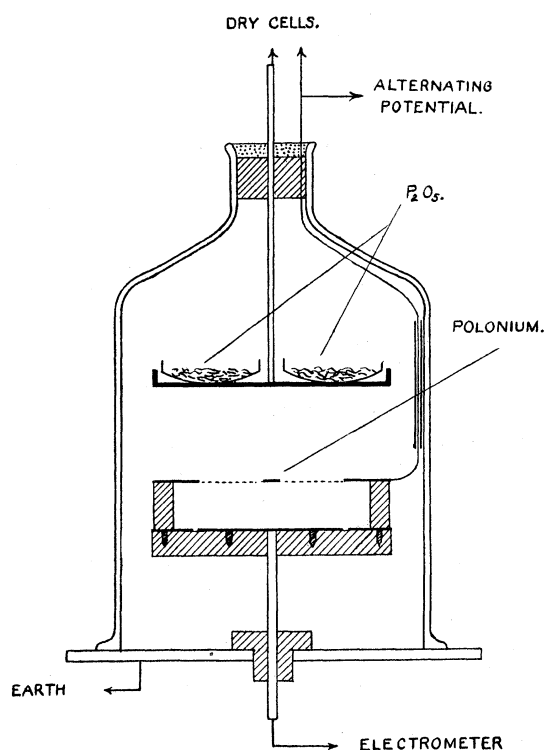


Fig. 1. Apparatus for determining mobilities by the Rutherford-Franck method.

mean height 2.494 cm, the three differing only slightly in the last figure. The pillars stood at the outer edge of the guard-ring, and a minute trace of seccotine was used to fasten them in position. The rim of the gauze rested on them without any adhesive.

The source of ionization was a deposit of polonium on the central portion of a small disk of bismuth which rested on the centre of the gauze. At a distance of 5 cm above the gauze was a parallel plate and between this and the gauze a steady potential difference was maintained by means of dry cells. In most of the work to be described subsequently, the value of this potential difference was 50 volts. The plate was fitted with a small

rim and was used to support porcelain dishes containing phosphorus pentoxide when drying was desired. The plate was supported by a rod passing out through an ebonite plug which served as a stopper in the glass bell-jar which surrounded the apparatus. A wire making connection with the gauze was brought out through the same plug. Part of the wire inside the vessel was surrounded by a thin glass tube. The bell-jar was 16.5 cm in diameter internally. It was ground on to the iron base-plate, the contact being made air-tight by the use of a little vaseline. The ebonite plug in the neck of the bell-jar was sunk about $\frac{1}{2}$ cm and the space flooded with molten paraffin wax.

The alternating potential was derived from the secondary of a transformer, one terminal of the secondary being earthed and the other connected to the gauze through a 2-volt cell. The cell was so connected that the upward field on the ions was slightly greater than the downward, so that ions which had just escaped capture at the plate were discharged by the gauze, or at least compelled to traverse the full upward distance before the next alternation of the field. The primary of the transformer was connected to the Dublin supply, the frequency of which is about 52. The voltage of the secondary, which could be readily varied by varying the resistance in the primary, was read off directly on an Ayrton and Mather electrostatic voltmeter. Two of these were used; one having the range 80-250 volts could be read accurately to $\frac{1}{2}$ volt, the other having the range 200-600 volts could be read accurately to 1 volt. The frequency was measured at the beginning and end of each set of observations and was remarkably steady. The electrometer used was of the Dolezalek type with quartz insulation and a phosphor-bronze suspension. Its sensitivity was about 1000 mm/volt and the capacity of the electrometer and apparatus was 165 cm.

VARIATIONS IN APPARATUS

Gauze. A number of sets of observations were made with a perforated brass plate substituted for the gauze. The plate was quite flat, 1 mm in thickness and had 12 circular holes per cm^2 , each 2.35 mm in diameter. The results did not differ in general character from those obtained with the gauze except that the currents to the lower plate were considerably smaller. It is evident that a smaller number of ions found their way through the perforated plate.

Vessel. In about half of the observations a metal enclosure was used instead of the glass bell-jar. The dimensions were almost exactly the same except that the top was flat. In this case the connection to the gauze was brought out through the iron base-plate. As will be seen later, the essential character of the results was not affected by these modifications.

Apparatus for hydrogen. The apparatus used for observations on hydrogen,² which was also used for some work on air, differed from that described only in dimensions. The electrometer-plate was 10 cm in diameter and the guard-ring 15 cm. The height of the pillars was exactly 4 cm. The apparatus was enclosed in a brass vessel 20 cm in internal diameter.

CONDITIONS FOR ACCURATE OBSERVATIONS

Constancy of ionization. This is secured by the use of polonium. From some points of view, ions produced photo-electrically are preferable, since any uncertainty as to conditions at the grid is avoided. On the other hand, one is limited to negative ions, and, a more serious matter, steadiness of ionization is difficult to attain.

Constancy of alternating field in amplitude and frequency. This is most likely to be attained from a large a.c. system such as that of the Dublin public supply. Except at certain hours of the day, the voltage as recorded by the voltmeters was remarkably steady. The practice was adopted of working during intervals in which previous experience had shown that the voltage was undisturbed. As far as may be judged from the voltmeter readings, the voltage on favorable occasions was steady to at least $\frac{1}{2}$ per cent. The curves obtained bear out this view. The maximum change of frequency noted from day to day was of the order of 1 per cent; the maximum variation between the beginning and end of an experiment was about 2 parts in 500.

Parallelism of gauze and plate. The distance between the gauze and the plate enters into the formula for the determination of mobility in the second power. It is obviously of great importance that exact parallelism should be secured. The apparatus used by the author has been specially designed in order to make sure of this point. In the form of apparatus used by Loeb, strict parallelism is very difficult to obtain. Loeb estimates an uncertainty in his mobility values of ± 3 per cent on this account.

Uniformity of field. The guard-ring should effectively eliminate any distortion of the field due to the walls of the vessel. The fact that the substitution of metal for glass made no difference in the results shows that the protection is effective. It readily appears from calculation that the density of ionization used will not appreciably disturb the field. There remains the possibility which has been suggested⁵ of penetration of fields through the gauze. If the lines of force from the upper (accelerating field) penetrate through the gauze in any numbers, one would expect to find a current to the lower plate when the gauze is at earth. An effect of this

⁵ Miss Zimmerschied, Phys. Rev. **21**, 721 (1923)

character has been noted previously³ and a different explanation suggested. This effect appeared only when the intensity of ionization was high and when the gas was very dry. It has not been observed in the course of the work dealt with in this paper.

Induction effects due to the alternating field. Various devices are employed by different workers in order to eliminate this cause of disturbance to the electrometer system. The simplest method is to disconnect the electrometer from earth *before* closing the primary circuit of the alternating system. The inductive effect is then almost negligible and the electrometer needle soon takes up its uniform rate of motion.

Insulation. It is essential that the insulation of the electrometer system should be good. The test of insulation applied was that the electrometer and plate should not leak more than 5 divisions per minute when charged to .14 volt, no condenser being in parallel.

RESULTS OF EXPERIMENTS

In Fig. 2 are plotted some of the current-voltage curves obtained with negative ions. Curve A is the result of some observations made on air saturated with water-vapor. The lower part of the curve was obtained with a condenser of capacity .001 mf in parallel with the electrometer, the upper part with a capacity of .003 mf. The readings with the higher capacity were multiplied by the appropriate factor to make them correspond to the readings with the lower capacity. The two sets of observations overlap between 470 and 490 volts. It is not possible with any pretence to accuracy to draw through these points a smooth curve cutting the axis sharply. A nearer approximation represents it as a number of straight lines intersecting at 520, 474 and 435 volts. The constant (mobility \times critical voltage) was 710. The curve therefore represents ions of mobilities 1.36, 1.50 and 1.63, corresponding to three of the ions to which the author attributes the bulk of the ionization in moist air. The curve shows the presence of another ion, but the intercept with the voltage axis is not sharp enough to allow of its mobility being calculated. Now it is not contended that the curve given is a simple composite of four curves, one for each kind of ion. It will be seen later that close examination would show it to be more complex. But it does show that the bulk of the ions in moist air tend, as has been claimed in previous papers, to fall into four principal groups of which three are here indicated.

A remarkable confirmation of this result has been found in the cloud experiments of C. T. R. Wilson.⁶ In one photograph, the separation in an electric field of the four kinds of ion produced in the track of an α -

⁶ C. T. R. Wilson, Proc. Camb. Phil. Soc. 21, 405 (1923)

particle is shown by four parallel cloud-tracks. It is difficult to conceive of any possible explanation of this photograph other than the four-fold character of the ionization.

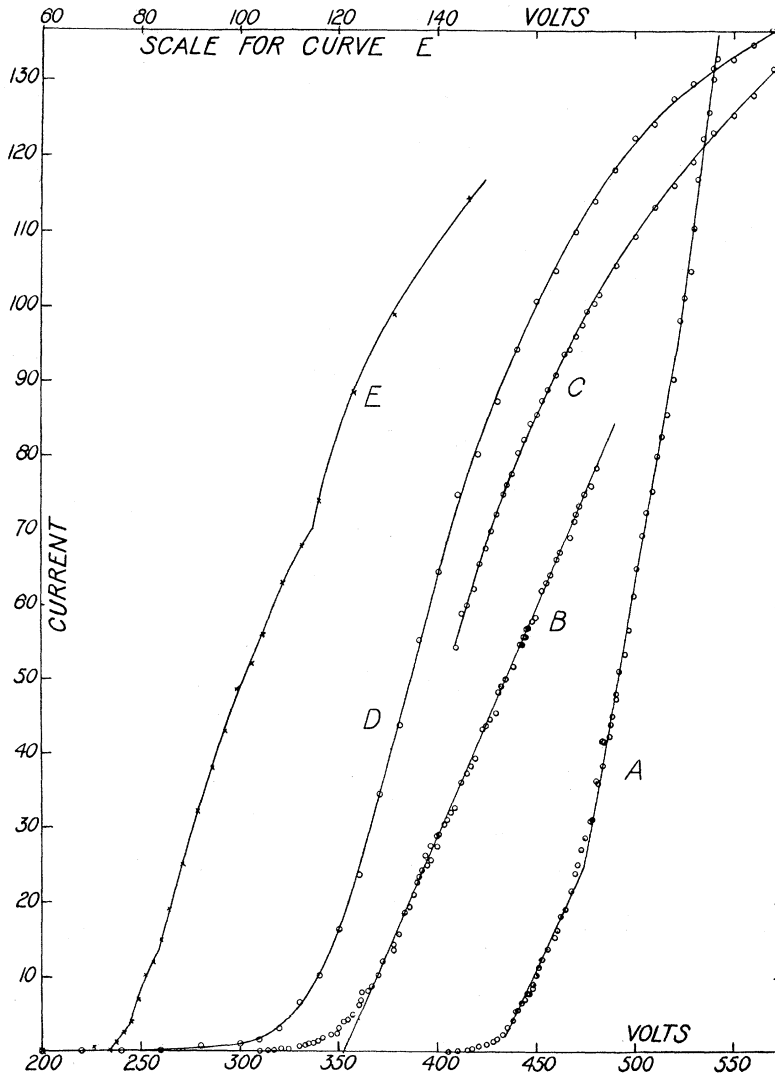


Fig. 2. Current-voltage curves
A, saturated air; B, air partially dried; C and D, dry air; E, Loeb's curve.

In the work described in the present paper, the interest was not so much in the ionization in moist air as in the changes produced by drying and the accurate estimation of the mobilities of the faster groups of ions.

Porcelain dishes containing phosphorus pentoxide were inserted and the vessel was sealed up. Two days after the drying began Curve B was obtained. The upper part of this curve was taken with a capacity of .008 mf in parallel with the electrometer, the lower parts with .003 and .001 mf. The overlapping parts agree very well except for some observations between 390 and 400 volts. The ordinates of this curve (and of Curves C and D) should be multiplied by 2.67 for comparison with Curve A. If what Loeb calls the "asymptotic foot" at the bottom of the curve be disregarded, a straight line may be drawn through the plotted points. This line intersects the voltage axis at 352, and it might be said that the observations therefore indicate the existence of a single ion of mobility $710/352 = 2.02$. But in the opinion of the writer, this summary treatment does not reveal the true conditions. In the first place the asymptotic feet in these curves cannot be so lightly disregarded; and in the second place, the straight-line part of the curve will, if attentively examined, show a remarkable peculiarity. It has a gapped appearance due to the fact that while the observed voltages are fairly uniformly distributed, the current values show sudden jumps at regular intervals. In the spaces between the gaps, the current values, while never very far from the straight line, exhibit a tendency to lie first above and then below it. In fact it would seem that the curve is not a straight line but a series of short curves, each short curve corresponding to a step of about 10 volts. It might be alleged that this appearance is quite illusory; that the regularly occurring curvature is due to some experimental error—some error in reading the voltmeter for example. Now it will be shown later when the curve is examined closely and not in the rather crude fashion just given, that this complex structure can be quite definitely and accurately established. On the other hand, Curve C which was obtained with very dry air, is plotted to show that at a higher degree of drying the upper part of the curve is quite smooth. If the form of Curve B is due to experimental irregularities of any kind, they should equally well affect Curve C, for the only difference is that one curve was plotted 40 days later than the other.

In order to compare the results with those obtained by Loeb, Curve D has been plotted. This curve was obtained 23 days after drying had begun, that is 21 days after Curve B. All observations were taken with a condenser of .008 mf in parallel with the electrometer. Curve E has been plotted from Loeb's observations taken from Fig. 3 of his paper. The points have been taken from an enlarged photograph of Loeb's curve and it is believed that they are accurately reproduced. While in general outline there is not much difference between the author's curve and that

of Loeb, it will be noticed that the latter is not of as regular a character. Loeb draws a smooth line through his points, but the author has ventured as the diagram shows, to follow the points rather more closely. Possibly Loeb's observations are inaccurate owing to want of steadiness in the ionization and want of parallelism in his apparatus, but as he states that each point was obtained from the average of two concordant electrometer readings, it may be assumed that inaccuracy on the first head at least has been eliminated. This being so, the author cannot find any reason for refusing to give to Loeb's experimental points their full value, especially as they can be made to lie accurately on a number of smooth curves instead of very inaccurately on one. There can be no doubt whatever that Loeb's curve shows a bend at 115 volts. It also shows but not so strikingly, bends at about 83.5 volts and 78 volts and there is a slight indication of a sag in the curve at about 103 volts. Loeb's mobility constant was 169 approximately. Therefore his curve shows quite distinctly the ion of mobility $169/115 = 1.47$, also ions of mobility 2.02 and 2.17. It shows indications of a possible ion of mobility about $169/103 = 1.64$. It is hardly necessary to point out how closely these results agree, not merely in general character, but in the actual values of the mobilities with the results published by the present writer. The curve for dry air (D) is much smoother than that of Loeb, but seems to have the "asymptotic foot" better developed. It is, in fact, what the author is accustomed to regard as the characteristic curve for a dry gas, while Loeb's curve is intermediate in character between that for a dry gas and that for a saturated gas (A). In other words, the drying in Loeb's case seems to have been imperfect. The question of drying is not a simple one, but the work of Baker⁷ and others seems to show that the gas in a vessel cannot be dried by simply filling it through drying materials. Prolonged contact of the gas with the drying agent is necessary.

Loeb's other curves (Figs. 1 and 2 of his paper) are not so well suited for comparison, principally because they show too small a number of points over the range under discussion. Inside that range, however, they certainly show irregularities of such a character as to suggest that if more points were determined the complex character of the curves would be disclosed.

The Curves A to D have been plotted only to show that there is no divergence between the author's results and those of Loeb so far as the latter has gone, and that it is not necessary to seek for explanations of differences which have not been proved to exist. Curves of this char-

⁷ Baker, *Jour. Chem. Soc. (London)* **81**, 400 (1902); **101**, 2339, (1912); **121**, 568 (1922)

acter have been regarded by the author as only in the nature of preliminary surveys of the ground. The real investigation consists in the close scrutiny of the current-voltage curve stage by stage.

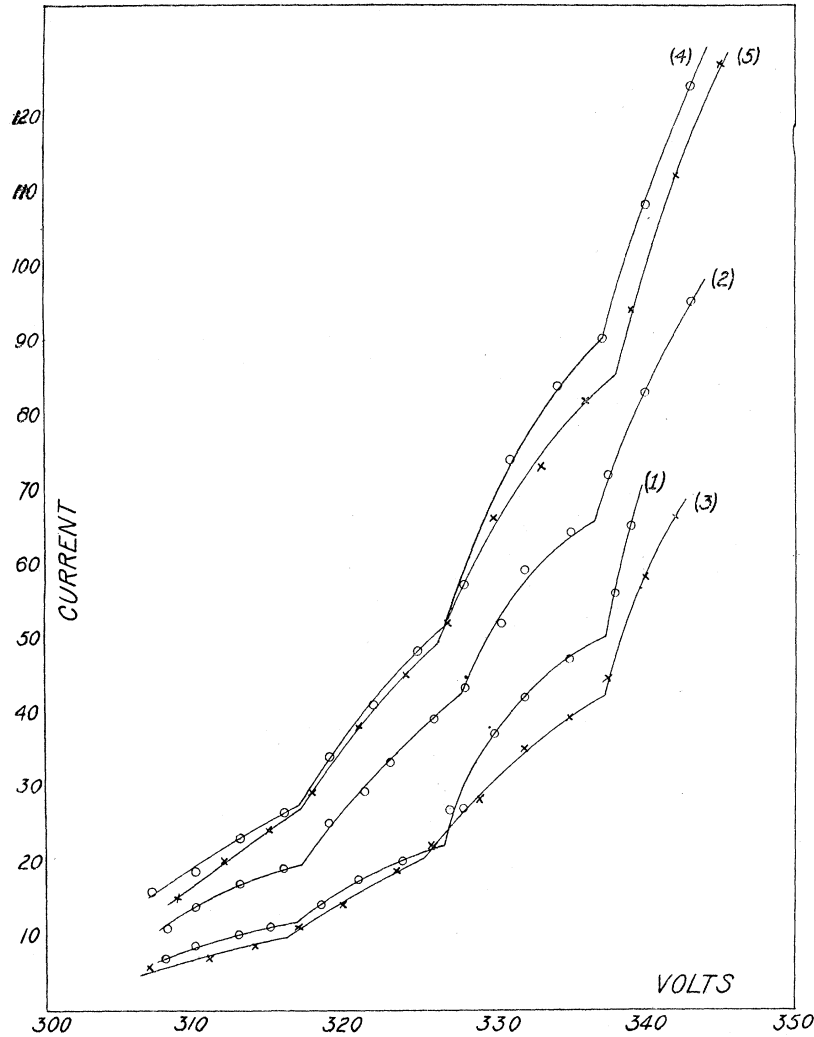


Fig. 3. Current-voltage curves for 300-350 volts, at different stages of drying.

ACCURATE INVESTIGATION OF THE STRUCTURE
OF CURRENT-VOLTAGE CURVES

In Fig. 3 a number of curves are plotted showing the examination of the current-voltage curve over the range 310-345 volts, that is, corresponding to the rounded portion at the foot of Curve D. Curve 1 was

plotted two days after drying had begun, that is on the same day as Curve B. The currents over that range of voltage were then small so that no auxiliary capacity was used. Curves 2 and 3 were plotted after 16 and 25 days drying respectively. Here and also in the case of Curves 4 and 5, a condenser of .001 mf was used in parallel with the electrometer. For purposes of comparison with the other curves, the ordinates of Curve 1 should therefore be divided by $6\frac{1}{2}$. While the effect of drying as shown by Curve 2 has been to produce a big increase in the current values, this increase had not been maintained in Curve 3—in fact there is a considerable reduction. From this and other evidence it was concluded that drying was not going on at a satisfactory rate; certainly not as rapidly as in previous experiments.³ It was thought possible that the difference was to be attributed to the glass vessel as metal only had been used in the previous work in which a high degree of drying was shown by the rapid appearance of ions of high mobility. The problem is perhaps not so much to dry the gas as to dry the walls of the vessel. A metal vessel was therefore substituted for the glass bell-jar, fresh P_2O_5 was introduced and the apparatus sealed up once more. Curves 4 and 5 were obtained with the new apparatus 31 and 39 days later. These curves, which are very nearly identical, show a considerable increase in current values over those obtained with the first apparatus, but even in this case it is believed that a really high degree of drying was not reached. It is probable that there were minute leaks in the apparatus and that moist air from outside found its way in.

The curves which have been reproduced in Fig. 3 are selected curves only in the sense that curves have been picked which cover the whole range. Every electrometer observation has been plotted. These curves as well as the much greater number which have not been given, agree in showing that the current-voltage curve is made up of a number of curves, convex upwards, showing intersections at 317, 327 and 337.5 volts. In the absence of any explanation of how a periodic character could be impressed upon the curve by any property of the field, of the grid or of the recording instruments, there is no escape from the conclusion that each intersection represents a distinct group of ions.

In Fig. 4 are given six curves covering the range 340-385 volts. As before, these curves represent different stages of drying, the lowest curve having been plotted 1 day after drying began. All curves are plotted to the same scale. Only one of these curves (the short curve on the left-hand side) was obtained with the apparatus in the metal enclosure. All curves agree in showing discontinuities at 348, 358.5, 368.5, and 378.5 volts. It is

hardly necessary to point out that if only a few widely spaced observations are taken, the true nature of the curve will not be disclosed.

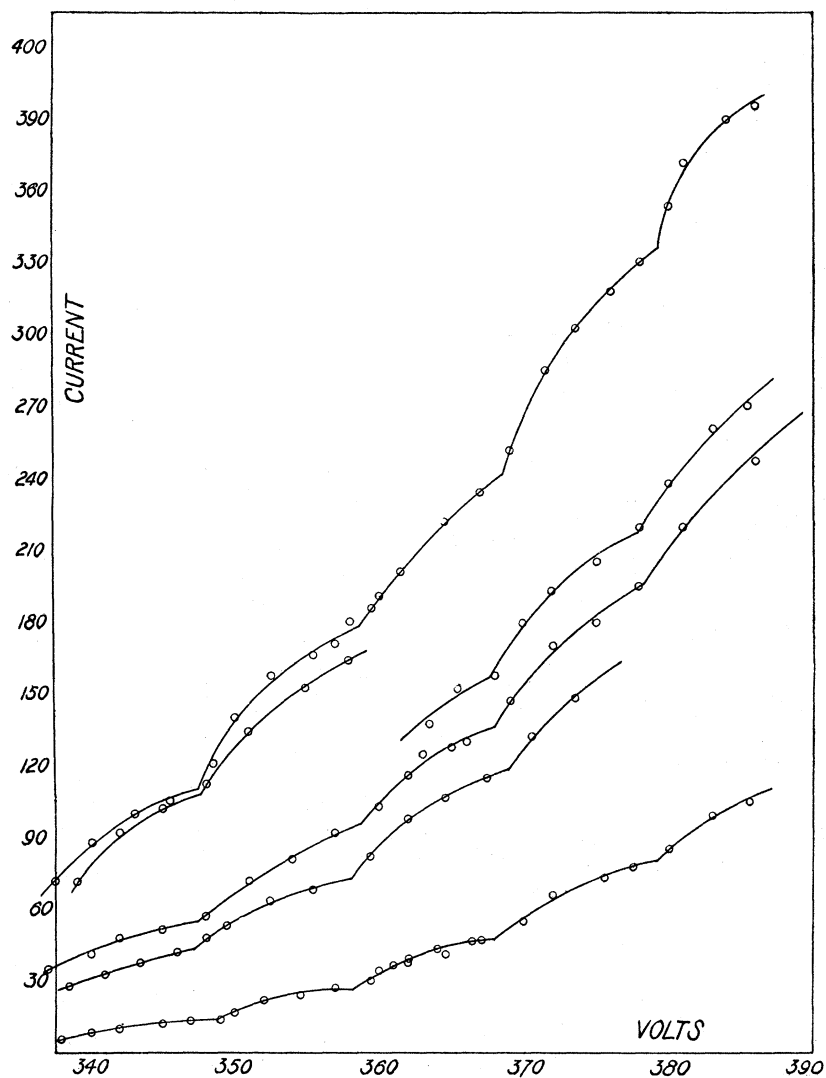


Fig. 4. Current-voltage curves for 340-390 volts, at different stages of drying.

From the accurately established critical voltages the following mobility values are deduced:

Critical Voltage	Mobility
317	2.24
327	2.17
337.5	2.10
348	2.04
358.5	1.98
368.5	1.93
378.5	1.87

It is not proposed in the present paper to deal in detail with the examination of the curves for higher or lower mobilities than those just given. The values for the mobilities of the faster ions are not yet all definitely known, and what is perhaps more important, the number of groups intervening between the fastest given above (2.24) and the ion of mobility about 12 (which the author regards as the mono-molecular ion) is still slightly uncertain. Judging from the best and most recent experiments, the first three ions have mobilities about 11.5, 7.5 and 6 and there appear to be ten or eleven other ions intervening between these and the fastest ion given in the table. As regards the slower ions there is ample evidence. Curve B has already shown that there is an inflection for about every 10 volts between 250 and 470 volts. Thus the list above can be continued giving critical voltages at about 390, 400 etc. to 470 volts. This is amply confirmed by observations taken over this range with both positive and negative ions. Accurate observations show that the critical voltages should be approximately 388, 398, 408 etc. and that this succession continues up to 528 volts and beyond it. Of course, if the air is very dry, Curve C shows that the slower groups do not appear.

The author interprets these results in terms of a theory of the constitution of the ion put forward by him some years ago.⁸ According to this theory the ion is a cluster of water molecules containing any number of molecules up to 30 or 40. Any size of cluster may be present depending on the conditions; for example in moist air four types are generally found. Drying tends, especially in the case of the negative ion, to eliminate the larger clusters and to bring the smaller ones into prominence. In the original paper the author suggested that the four kinds of ion ordinarily prominent in moist gases contained 18, 24, 30 and 36 molecules of water respectively. The mobility of these four hypothetical ions was calculated using a formula due to Sir J. J. Thomson. The value found for the mobility of the ion composed of 30 water-molecules was 1.53. This ion is usually very prominent; Loeb's Curve E shows it having mobility 1.47 and Curve A shows it having saturation voltage 474 and mobility 1.50. The close analysis of the curves shows that the correct saturation voltage should be 468 (mob.=1.52). If our view as to the constitution of the ions is correct, the next slower ion—critical voltage 478—has 31 molecules of water, the next 32 and so on. If we continue in this fashion we find that the ion of 36 water-molecules should be disclosed at critical voltage 528. This is a notably prominent ion in all curves taken with moist air. Its mobility is 1.34, which corresponds with the calculated value 1.31. Its

⁸ J. J. Nolan, Proc. Roy. Soc. **94**, 112 (1917)

prominence is shown by Curve A, which gives its mobility as 1.36. On the other hand, going from the ion of 30 water-molecules to the smaller ions, we find that the ion indicated by the critical voltage 408 should have 24 water-molecules. Critical voltage 408 gives mobility 1.73; the mobility calculated by the author for an ion of 24 water-molecules is 1.72. Continuing in the same way, the ion indicated by the critical voltage 348 should have 18 water-molecules. Mobility determined (see table) = 2.04; mobility calculated = 1.97. The fastest ion in the table should have 15 water-molecules; the value calculated is 2.17, the value found is 2.24. There should then be 14 possible ions left; it has been already stated that that number, or possibly one less than it, have been found.

The numbers (18, 24, 30 and 36) originally suggested for the more prominent ions were chosen because they fitted the results of experiment better than any others. "With fuller information the ions might be better represented in terms of some other unit rather than six."⁸ There would now seem to be considerable justification for believing that the numbers originally suggested cannot be far wrong. Apart from the evidence just given, the work on gaseous hydrates⁹ which shows that bodies of the type $M(H_2O)_6$ are readily formed, even when M is a molecule of such a gas as argon, is highly significant in this connection.

DISCUSSION

The author has in previous papers shown by various methods that the ions in moist air fall into four distinct groups. Direct confirmation of this has been found in the work of C. T. R. Wilson. It is now possible by refined observation to follow the building up of the ions constituting these groups and to detect the less prominent intermediate stages. The number of intermediate stages found is in accordance with the number of molecules previously assigned to each ion. The smaller ions, when brought into prominence by extreme drying, afford further confirmation by their absolute mobility values and by their spacing. For many reasons it is believed that the unit out of which the ions are built is the water-molecule.

Apart from the evidence brought forward in this paper, the theory which regards the ordinary ion as a charged gas-molecule is quite untenable. When the author originally found¹ an ion of mobility 12.5 in the air ionized by the decay products of radium, he was unaware of the results of Franck,¹⁰ Altberg¹¹ and Moore.¹² Franck found a negative ion

⁸ See Bouzat, C. R. **176**, 253 (1923), and de Focrand, C. R. **176**, 355, (1923)

¹⁰ Franck, Ann. der Physik **21**, 972, (1906)

¹¹ Altberg, Ann. der Physik **37**, 849 (1912)

¹² Moore, Phys. Rev. **34**, 81, (1912)

with a mobility of 12.26 in dry air; Altberg found a negative ion of mobility 10.1 and Moore found a negative ion of mobility 9.72. The agreement is good considering the great differences in the methods employed by these workers. That this is the true monomolecular ion can hardly be doubted. The values found for the fastest positive ions by these workers are respectively 3.22, 7.5 and 6.43. Again, the present writer can find no reason for refusing full credit to the results of Haines¹³ on hydrogen; his own observations confirm those of Haines and he has recently in dry hydrogen found Haines's ion of mobility 40.6. Finally, the fact that the recoil atom has about the same mobility as the ordinary positive ion is fatal to the "small-ion" view, unless a form of theory is invoked which would make the mobility independent of the mass. Even this very questionable alternative is ruled out by the observations of C. T. R. Wilson⁶ who has obtained photographs showing definitely that the atom of ThA was displaced twice as far by an electric field as the ordinary ions in the same time. The fact that a body of mass 216 can move twice as fast as the ion under an electric field, shows not only that the ion is a cluster, but that it is a cluster containing a considerable number of molecules.

The author is indebted to Mr. P. B. Carolan from whose observations the curves in this paper were plotted. It is hoped to publish the results of Mr. Carolan's observations more fully on a subsequent occasion, especially those dealing with ions of high mobility which have been only lightly touched upon in this paper.

UNIVERSITY COLLEGE, DUBLIN.
December 8, 1923.

¹³ Haines, *Phil. Mag.* **30**, 503, (1915) and **31**, 339, (1916)