THE
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THE MOBILITIES OF GASEOUS IONS.*

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PART I. METHOD AND PROCEDURE.

I. *Introductory Statement.*

“IN spite of the great number of investigations devoted to gases during recent years the question whether an ion is a molecule or an atom carrying an elementary charge, or whether it is a number of neutral molecules clustering about a charge is not as yet definitely settled.”¹ So wrote Franck eight years ago. Even now in spite of all the researches carried on along the same line since then the question is by no means settled, for its various solutions are far from being universally accepted.²

When the phenomenon was revealed that the mobilities and the diffusion coefficients of the ions in gases were relatively small in comparison with those of the uncharged molecules, the first hypothesis formulated for its explanation was that each individual ion, instead of being a single charged molecule, was a cluster of neutral molecules around an elementary charge.³ Thus the ion, being a cluster of molecules had a mass greater than that of a single uncharged molecule, and consequently would move more slowly than the latter under similar conditions. Later, in 1909, Wellisch⁴ and Sutherland⁵ offered another hypothesis

* Presented at the Chicago meeting of the Physical Society, December 1, 1917.

¹ Franck, *Verh. der Deut. Phys. Ges.*, 11, 397, 1909. Über die Ionenbeweglichkeit der radioaktiven Restatone und die Masse des Gasionen.

² An idea of the extent of the work on this subject may be had by adding to the list of references given by J. Franck in his article “Bericht über Ionenbeweglichkeit,” *Jahrbuch der Radioaktivität*, 9, 235, 1912, the following: Townsend and Tizard, *Proc. Roy. Soc., A*, 87, 1912; *A*, 88, '13; Moore, *Phys. Rev.*, 1912; Todd, *Phil. Mag.*, 1913; Wellisch, *Am. Jour. Sci.*, May, 1915; *Phil. Mag.*, March, 1916; Haines, *Phil. Mag.*, 30, 1915; 31, 1916; Loeb, *Phys. Rev., N. S.*, VIII., No. 6, 1916.

³ Rutherford, *Radioactive Substances and their Radiation*, p. 56.

⁴ E. M. Wellisch, *Trans. Roy. Soc., A*, 209, 1909.

⁵ W. Sutherland, *Phil. Mag.*, 18, 341, 1909.

for the explanation of the same phenomenon. In opposition to the older assumption of the "cluster" they claimed the ion to be a single charged molecule and its low mobility to be a consequence of the retardations along its path through the gas by virtue of the charge it carried. The charge of the ion would attract the uncharged gas molecules and thus would cause it to collide more often with the latter than would an uncharged molecule in traversing the same distance. Thus the relatively slower mobility of an ion was ascribed by one hypothesis to the increase in its mass and by the other to the increase in the number of collisions with the gas molecules; and both explanations were equally plausible.

The contradictory and rival hypotheses once having been adopted, their verification was in order. Their possible consequences were made the best possible criteria of their verification. It was reasoned that if the ion was a cluster of neutral molecules about an elementary charge, either an electron or a positive corpuscle, it would break up as soon as it had acquired a kinetic energy sufficiently high to cause such an effect. This disintegration of the ion would result in a decrease of its mass; in accordance with the hypotheses this decrease would manifest itself in an abnormal increase of its mobility. On the other hand, if the ion was a single charged molecule—a "small ion"—it would not disintegrate, and consequently its mobility would remain constant.

Thus, the measurements of the mobilities of ions were considered the best methods for the verification of both the "cluster" and the "small ion" hypothesis. For if the mobilities were found to increase abnormally when a high kinetic energy was imparted to the ions, and if this increase could not be attributed to anything other than the increase in the kinetic energy, then the "cluster" nature of the ions would be positively established. But if the mobilities did not increase even after the ions had gained a high kinetic energy, the "small ion" hypothesis would be verified. Hence the ions were caused to travel under electric field and at pressures designed to impart to them enormous velocities. If the ions remained intact—if no disintegration occurred—their velocities would be proportional directly to the field strength and inversely to the pressure. But if the "cluster" dissociated, the proportionality would not hold.

Early experiments along the general direction described led to varied and conflicting results. Latty,¹ Kovarick,² Todd,³ Townsend⁴ and Franck⁵ obtained abnormally high mobilities whereas Chattock⁶ and

¹ R. F. Latty, *Proc. Roy. Soc., A*, 84, 1910.

² A. F. Kovarick, *PHYS. REV.*, 30, 415, 1910.

³ Todd, *Phil. Mag.*, S. 6, Vol. 22, p. 791, 1911; *Phil. Mag.*, June, 1913.

⁴ J. S. Townsend, *Proc. Roy. Soc., A*, 85, 1911.

⁵ J. Franck, *Ann. der Physik.*, 22, 972, 1906.

⁶ Chattock, *Phil. Mag.*, 48, 401, 1899.

Wellisch¹ found the mobilities to remain normal through a wide range of pressures and field strengths. The latest additions to the collections of data in support of the cluster hypothesis was the work of Moore,² and that of Haines;³ while the most recent additional proof for the small ion theory was embodied in the works of Wellisch⁴ and Loeb.⁵ The latest of the "cluster" exponents, namely Haines, even went a step further and maintained that the results of his experiments indicated not only that the ions were formed by clusters of molecules but also that the ions of the same gas—hydrogen being the case under consideration—were made up of the combination of molecules varying in numbers. Contrary to this Loeb's work with air at potentials of as high as 12,450 volt/cm. gave absolutely normal results.

Thus the facts as they stood apparently pointed in contrary directions. But it is only in keeping with modern experimental methodology that reasonable explanations be discovered for the apparently contradictory facts. It was for this reason that further work along this line was considered desirable; and hence the work herein described was undertaken.

All the observations, excepting those of Franck, Moore, and Loeb, employed only ordinary low potentials; and even the field strength employed by Franck and Moore, though higher, was merely roughly approximated. The method employed by Loeb in his work in air appeared to be the most definite and most direct method ever designed. And for this reason and for reasons that will become apparent later on, this method was adopted.

An attempt was first made to repeat Loeb's experiment with air under different conditions by increasing the frequency of the alternating field to nearly twice as high and the field strength by about fifteen per cent.

Then the mobilities of hydrogen ions were measured in fields varying from 9 to 6,669 volts per cm., and those of nitrogen ions in fields varying from 11 to 17,670 volts per cm.

The results, be it anticipated, indicated no tendency on the part of the ions to disintegrate; that is, the mobilities were found to be absolutely normal within the limits of experimental errors, and the law $Up = \text{constant}$, where U is the mobilities and p the pressure, was found to hold over the whole range of fields and pressures employed.

¹ E. M. Wellisch, *Am. Jour. Sci.*, May, 1915; *Phil. Mag.*, Mar., '16.

² Moore, *PHYS. REV.*, 1912.

³ Haines, *Phil. Mag.*, S. 6, Vol. 30, 1915; Vol. 31, 1916.

⁴ Wellisch, *Phil. Mag.*, July, 1917.

⁵ Loeb, *PHYS. REV.*, Vol. VIII., 633, Dec., 1916.

2. *The Method.*

The method here employed was the Rutherford¹-Franck² alternating potential method as employed by Loeb. It consists in the determination of the distance traversed by an ion (or rather by a number of ions) parallel to the direction of a known electric field during a half period of the alternation. From this distance d , the known potential E , and the frequency n , the mobility U was calculated from the formula:

$$U = \frac{\pi n d^2}{\sqrt{2} E}.$$

3. *The Apparatus.*

The apparatus here employed was essentially the same as that used by Loeb.³ In fact it was Loeb's apparatus modified in a few details to meet some mechanical criticisms which had made their way into the mind of the present writer. However, the general structure of the apparatus remained the same.

4. *Establishment of Potential.*⁴

The low-frequency alternating field employed was obtained from the ordinary city supply. The high-frequency field was established by an oscillating circuit in which the oscillations were generated by a Chaffee Arc.⁵ By way of supplementing Loeb's account, it may be pointed out here that the desired high-frequency oscillation potential was obtained by the application of the following formula for syntonized coupled circuits:

$$\frac{V_2}{V_1} = - \frac{\sqrt{C_1}}{\sqrt{C_2}},$$

where C_1 and V_1 represent the capacity and potential across the condenser plates—of one circuit, and C_2 and V_2 the capacity and potential of the secondary circuit. From the above formula and from the familiar formula $C_1 L_1 = C_2 L_2$ it can be seen that with a given primary circuit $C_1 L_1$ and a variable circuit $C_2 L_2$ it will be necessary to increase L_2 and decrease C_2 in order to increase the potential across C_2 and at the same time to keep the circuits syntonized, or, to be exact, almost so.

The most important condition to be satisfied here was that the potential

¹ Rutherford: *Proc. Camb. Phil. Soc.*, IX., 410, 1898.

² J. Franck: *Ann. d. Phys.*, 21, 985, 1906.

³ See Loeb, *loc. cit.*, for description.

⁴ See Loeb, *loc. cit.*, for description.

⁵ E. L. Chaffee, *Proc. Am. Acad. Arts and Sci.*, Nov., 1911.

⁶ See J. A. Fleming, *The Principles of Electric Wave Telegraphy and Telephony*, 3d ed., p. 302, 1916.

might be as high as could be obtained provided the frequency was neither too high to render the critical distance d equal to or smaller than the sparking distance between the gauze and the collecting plate, nor too low to render the critical distance greater than that up to which the uniformity of the field between the gauze and the plate could be maintained.

Since

$$U = \frac{\pi n d^2}{\sqrt{2E}};$$

$$\therefore d^2 = \frac{UE\sqrt{2}}{\pi n};$$

$$\therefore d = \sqrt{\frac{UE\sqrt{2}}{\pi}} \bigg/ \sqrt{n}.$$

Thus, for a given potential E , assuming the mobility U to be constant, the critical distance d is inversely proportional to the square root of the frequency n .

But the sparking distance d is directly proportional to the potential E , say $d = KE$.

Comparing this equation with that just derived above, namely,

$$d = \sqrt{\frac{U\sqrt{2}E}{\pi n}},$$

it can be easily seen that if

$$n \equiv \frac{U\sqrt{2}}{\pi K^2 E},$$

sparking would occur across the gauze and the plate before they were brought sufficiently close to each other in order to enable the ions streaming from the gauze towards the plate to reach the latter before the sign of the potential was reversed.

On the other hand if n was so small as to render d too large, the gauze and the plate would have to be very far from each other in order to reach the critical distance. This would destroy the uniformity of the field between the plate and the gauze. Besides, the critical distance might be beyond the range of the apparatus.

There was also a practical limitation in this connection. If the potential was too high there would be brush discharges from the edges and corners inside the chamber, and this would give rise to serious disturbances.

The arrangement found to be satisfactory in this work was that which gave a potential of 5,000 volts at 14,758 cycles per second. This rendered the critical distance, especially that for nitrogen, very near to the sparking distance.

5. *The Determination of Frequency.*

The frequency of the alternating field employed was determined by photographing from a revolving mirror the sparks jumping across r when the balls were brought sufficiently close to each other. As it was necessary to keep the capacity of the circuit as nearly constant as possible, so that the frequency measured from the spark might be the same as that at which the mobility measurements were made, the spark gap r was kept in the circuit all the time. During the mobility measurements the gap was adjusted slightly wider in order to prevent sparking from occurring across it.

A camera with a Cooke anastigmatic lens, $f = 3.5$, was used. The photography was done in three different ways; first by clamping the camera on the table before the revolving mirror, then by sliding the camera up a vertical stand, and then by sliding the negative holder up, with a known speed, behind a lens fixed before the mirror.

The last method was developed under the impression that the first two were not accurate enough, but the results proved the inaccuracy of the two methods to be negligible in comparison with the other sources of error. However, the mechanical superiority of this method justifies a brief description.

Fig. 1 represents the essentials of the arrangement. Before the re-

Fig. 1.

volving mirror M was a light-proof box B with a lens L in the front, and a plate holder P sliding up and down at the back. When in operation P was pulled upward by a cord c passing over the pulleys p , p , and attached to the wheel W . The arrow in the figure indicates the direction in which the beam of light from the spark reached the photographic plate. Both the revolving mirror M and the wheel W were geared to a small

electric motor. When in operation the plate registered a horizontal series of sparks at each revolution of the mirror. Thus the time taken for P to traverse a distance equal to that between two successive series of images was the same as the time for M to make one revolution. And by measuring the speed of the mirror and that of the plate independently by direct measurements, the results served to check each other, and the time t taken for one revolution of the mirror could be obtained with great accuracy.

In view of the fact that the maximum potential was only $5,000 \times \sqrt{2}$ volts, the sparks were not very intense when the mirror M was placed from two to three meters away from the gap. Thus a powerful lens was necessary to render the images noticeable.

The distance between two successive sparks was determined by photographing on the same plate, when both M and P were at rest right after the photographs of the sparks were taken, a horizontal scale inserted between the gap with its length at right angles to the straight line joining the gap and the center of the mirror. Thus the image of this scale on the same plate with those of the sparks enabled the actual—and at the same time the apparent—distances between the latter to be determined directly.

From the time t , of one revolution of the mirror, the distance s between two successive sparks, and the distance D between the gap and the mirror, the frequency N of the sparks was computed by using the formula

$$N = \frac{4\pi D}{ts}.$$

As the frequency of the sparks was doubled the frequency of the alternating field we have

$$n = \frac{N}{2} = \frac{2\pi D}{ts}.$$

The average of twelve plates taken by the various methods previously described, and on several different occasions, with different D 's and t 's, gave the frequency mentioned elsewhere in this report.

6. *Measurement of Potential and Distance.*

The high-frequency oscillating potential was measured, while the determinations were being made, by a calibrated Braun electrostatic voltmeter having a range of ten thousand volts. The low-alternating potentials were measured at times by an ordinary General Electric voltmeter and at times by a calibrated Kelvin unicellular voltmeter.

The distance between the gauze G and the collecting plate P were measured by a cathetometer which gave them an accuracy of 0.1 mm.

7. *Mobility Determinations.*

In the determinations with high potentials the frequency and the potential were kept constant, and the distance between the gauze and the collecting plate was varied. The accumulated charges on the collecting plate for a chosen interval were communicated to the electrometer quadrants through platinum contact switches, and the deflections corresponding to the various distances between the gauze and the plate were recorded. A number of deflections were taken for each variation of distance.

The determinations with low potentials were made in two ways; by varying the distance keeping the potential constant, and by varying the potential keeping the distance constant. In both cases the electrometer readings were taken as above.

The electrometer deflections were plotted against either the corresponding distances or the corresponding potentials, and the critical distances or the critical potentials, as the case might be, were determined by finding the points of inflection on the curves.

The determinations of the positive and negative mobilities were made simultaneously by reversing the sign of the retarding field.

8. *Production and Purification of Gases.*

When the determinations were made in air the content of the chamber was first pumped out with a Pearson pump and fresh air was let in through a number of bottles containing concentrated sulphuric acid and a series of tubes containing calcium chloride and phosphorus pentoxide.

The hydrogen used was generated by a Kipp generator from HCl and zinc. It was passed successively through bottles containing KOH and concentrated H_2SO_4 , and tubes containing P_2O_5 and CaCl_2 , and then through two bulbs containing charcoal of cocoanut shell and immersed in liquid air, before its admission into the chamber. The chamber was revacuated and refilled three or four times before each set of readings were taken. This method, in all probability, produced, as far as the results have shown, very pure hydrogen.

The nitrogen employed in this work was produced by warming a mixture of sodium nitrite and ammonium sulphate. It was purified, before its introduction into the chamber, by its passage through solutions of KOH, FeSO_4 , and concentrated H_2SO_4 , and through tubes containing P_2O_5 , CaCl_2 , and heated copper. The content of the chamber was, as it was in the case of hydrogen, vacuated from three to four times before each set of readings were made.

PART II. RESULTS.

I. *Air*.

Fig. 2 shows a characteristic set of curves plotted from the measurements with air at atmospheric pressure (749 mm. of mercury). I. and

Fig. 2.

Air. I. and II. With $N = 14,758$ cycles; $E = 5,000$ volts; $P = 748$ mm.
 III. and IV. With $N = 60$ cycles; $E = 118$ volts; $P = 748$ mm.

II. were respectively positive and negative curves obtained with the high frequency oscillating potential of 5,000 volts. The critical distances were, as it may be seen on the curves, 0.5 cm. for the positive and 0.55 cm. for the negative ions.

Curves III. and IV. were obtained with the ordinary 60-cy. 110-volt alternating potential. 1.10 cm. and 1.25 cm. were taken as the critical distances for the positive and negative ions.

The results obtained for air are summarized in Table I. The first and second columns contain respectively the positive and negative mobilities computed from the formula,

$$U = \frac{\pi n d^2}{\sqrt{2} E},$$

deduced elsewhere in this report. The third and fourth columns contain the potential gradients calculated from the formula

$$X = \frac{\sqrt{2} E}{d}.$$

TABLE I.

Table of Results Obtained for Ionic Mobilities in Air, February-March, 1917.

1. 60 cy. 119 volts.

$U+$.	$U-$.	$X+$.	$X-$.	P .	$K+$.	$K-$.	R .
1.12	1.75	168	134	746	1.10	1.72	1.56
1.12	1.75	168	134	746	1.10	1.72	1.56
1.12	1.75	168	134	752	1.10	1.73	1.56
1.25	1.73	168	134	742	1.22	1.70	1.38
Mean.....					1.14	1.72	1.51

2. 14,758 cy. 5,000 volts.

1.64	1.98	14,160	12,870	752	1.62	1.92	1.21
1.57	1.84	14,160	12,870	750	1.56	1.82	1.17
1.64	1.98	14,160	12,870	749	1.61	1.95	1.21
1.57	1.84	14,160	12,870	746	1.55	1.81	1.17
1.82	2.10	13,810	12,650	692	1.66	1.92	1.17
2.26	2.61	12,300	11,550	558	1.66	1.91	1.16
Mean.....					1.61	1.90	1.18
Mean of both sets.					1.37	1.81	1.34

 $U +$ = Mobility of positive ions. $U -$ = Mobility of negative ions. X = Field strength in volt/cm. P = Pressure in mm. K = Mobility at 760 mm. pres. $R = K - /K +.$ $X -/P$ Max. = 20.70, Min. = 0.18. $X +/P$ Max. = 22.04, Min. = 0.22.

In the fifth column are the various pressures under which the determinations were made. K_1 represents the positive, and K_2 the negative mobility reduced to the pressure of 760 mm. of mercury. In the last column R , is found the ratio between the positive and the negative mobilities.

The potential used was as high as 14,160 volt/cm. for the positive and 12,870 volt/cm. for the negative ions. The maximum value of x/p was 20.70 for the negative ions and 22.04 for the positive.

The above results, as it may be seen, show that both the positive and the negative mobilities remained, within the limits of experimental error, absolutely normal, and thus no indication whatsoever could be found of there being any tendency of the ions of either sign to disintegrate under the potentials of the magnitude employed.

These results more than amply substantiated those obtained by Loeb in his work and it is therefore quite safe to conclude that the evidences obtained so far point in the direction of the "small ion" theory.

2. Hydrogen.

Fig. 3 shows a characteristic set of curves plotted from the measurements on hydrogen with the high-potential high-frequency oscillating field.

The peculiarity that distinguishes these curves from those previously obtained for air is the extension of the negative curves II., and IV.—one obtained under a pressure of 748 mm., while the other under 290 mm.—beyond the workable range of the apparatus. That this extension could not be the result of mechanical error is clear from the fact that the curves obtained for air under similar conditions showed no such extension, and even in the case of hydrogen the extension made its appearance only when the chamber was newly filled with gas directly from the generator

Fig. 3.

Hydrogen. I. and II. With $N = 14,758$ cycles; $E = 4,000$ volts; $P = 748$ mm.
III. and IV. With $N = 14,758$ cycles; $E = 4,000$ volts; $P = 290$ mm.
V. taken 7 hrs. after IV. was taken.
VI. with $N = 60$; $E = 118$ volts; $P = 748$ mm.

and through the purifying agents. When the gas was left in the chamber for some time this peculiar characteristic disappeared altogether. Curve V. (Fig. 3) was plotted from measurements on the same content, and under similar conditions, of course, as that from the measurements of which Curve IV. was plotted, except that the gas had been left in the chamber for about seven hours.

Again, this extension could not be attributed to the possibility that the gas had been charged when it was freshly prepared. In the first place, in the process of purification, the gas had to pass through twelve layers of glass-wool located in different parts of the purifying and drying agents. In the next place if the gas had carried any charge with it on entering the chamber the presence of this charge would have been indicated by the electrometer when the gas came in contact with the collecting plate. As the electrometer did not show any indication, it is only reasonable to conclude that the gas did not carry any charge at all when it entered the chamber.

3. EXISTENCE OF FREE ELECTRONS.

The most plausible explanation for this extension, therefore, must be sought in the existence of free electrons as was suggested by Wellisch.¹ On the basis of that hypothesis the deflections constituting the upper part of the curves II. and IV. may be interpreted to consist of the effects of both the normal negative ions and the free negative electrons, whereas those constituting the lower part of the curves may be conceived as due entirely to the free negative electrons. And such curves as those represented by V. may be said to be due entirely to normal negative ions. The ephemeral existence of these free electrons as proved by this latter case may conceivably be the result either of their fast dissipation into the walls of the chamber or of their ready formation of negative ions with the neutral molecules of either hydrogen or the impurities that found their way into the chamber in the meantime. Whichever way it might be, it is clear that these results indicate the existence of free negative electrons in hydrogen—at least in freshly prepared hydrogen.

4. *Existence of Other Species of Negative Ions?*

As mentioned previously, Haines² reported that he found two kinds of negative ions in hydrogen other than the normal negative ions. The existence of these ions was inferred from the fact that from the curves he obtained three different negative mobilities could be deduced. These

¹ Am. Jour. Sci., May, 1915; Phil. Mag., March, 1916.

² Haines, loc. cit.

mobilities were 40.6, 15.9 and 7.9 respectively. Thus from these mobilities he inferred that the number of hydrogen molecules constituting the positive and the three species of negative ions were respectively 9, 6, 3, and 1, at 76 cm. pressure and 15° C.

An effort was made to search among the results of the present experiment for premises from which the above mobilities could be inferred. And since, by virtue of the method employed, the inflections of the curves were the only ground on which computation of mobilities was based, the various curves were closely scrutinized to see if more inflections could not reasonably be found. Take Curve II. (Fig. 3) for example: if Haines's ions existed in the present experiment, there would be besides the inflection at the plate distance of 10 mm., two other inflections, one at about 14 mm. and the other at a distance of between 23 and 25 mm. As all

Fig. 4.

Hydrogen. With $P = 752$ mm.; $d = 2.0$ cm.; $N = 60$ cycles per sec.

efforts toward this end proved of no avail, it was concluded that either there were no such ions at all as Haines's *B* and *C*, or that they were actually present, only that the disposition of the apparatus employed was not sufficiently adequate for their detection. Furthermore, if it could be proved that these ions were not present the question still remained as to whether they were non-existent in general, or whether they did actually exist in Haines's but not in the present experiment.

On account of the above considerations the experiment was diverted to a slightly different direction. It was for the sake of the ratification of the method and apparatus thus far employed that an attempt was made to repeat Haines's experiment. Haines's experimental conditions were reproduced as exactly as possible according to his descriptions¹ with the expectations of obtaining similar results.

The results of this attempt were typified by the curves in Figs. 4 and 5. As it may be seen, there were striking similarities between these curves

Fig. 5.

Hydrogen. $P = 498$ mm.; $d = 2.0$ cm.; $N = 60$ cycles.

and those obtained by Haines from whose report Fig. 9 was copied; excepting the absence from the former of the inflections from which the mobilities 40.6 and 15.9 might be computed. The abundance of free electrons at the start manifested itself very markedly in all the curves obtained; and this would seem to vitiate all possible questions regarding the purity of the gas. The normal negative ions—namely those having the mobility 8.45 according to this experiment, or 7.9 according to Haines's—were distinguished by the definite inflections and intercepts of the curves.

Thus, these results agree with those of the employment of the high-frequency high-potential oscillating field in pointing to the conclusion that there were, in all probability, no other species of negative ions in hydrogen besides the one kind that were ordinarily found.

¹ Haines, Phil. Mag., S. 6, Vol. 30, 1915.

Perhaps it will be proper to mention here the fact that no sooner had the above conclusion been arrived at than it received corroboration from Wellisch's latest paper¹ in which it was reported that no trace could be found of Haines's ions *B* and *C*.

But how did Haines come to get these different mobilities? Such a question is not at all superfluous, since the spirit of experimental method demands a reasonable explanation for each and every apparent fact, and a mere denial or a conclusion to the contrary effect can no more explain away what had been considered fact than it can cause the earth to revolve in the opposite direction. A careful study of Haines's figures seemed to point to the possible ground on which some explanations may be based. The part of the curves below the point *A*, as it may be seen from Fig. 6,

Fig. 6.

Haines's curve for hydrogen, reproduced from *Phil. Mag.*, S. 6., Vol. 31, p. 340, Fig. 1, April, 1916.

which is a reproduction of his Fig. 1, shows irregularities which might very well be due to the fluctuation in the electrometer deflections caused by residual charges on the insulating material near the collecting plate. This source of disturbance was found in the present experiment to be the most troublesome, particularly when the high frequency oscillating field was employed. Besides, even without any promiscuous charges, fluctuations of some sort in the electrometer deflections were unavoidable, though they would not be so high, in most cases, to confuse the legitimate results provided proper precautions were taken; and no attempt was made to draw the curve to pass all the points. For instance, the portions of the curves in Figs. 4 and 8 corresponding to the parts of those in Fig. 7, in

¹ Wellisch, *Phil. Mag.*, S. 6, No. 199, p. 32, July, 1917. This number of the *Phil. Mag.* reached Ryerson Lab. just after the work was completed.

which the inflections *B* and *C* occurred, might be drawn in such a way as to have as many inflections as there were points; and with some imagination equally as many different mobilities might be deduced and hence as many kinds of ions might be inferred therefrom. But would these inflections be definite enough to justify the might-have-been conclusions? The answer seemed to be decidedly negative. A comparison of the inflections *B* and *C* with those designated by *A* in Haines's curves would conduce at once to the conclusion that the former were not sufficiently definite to justify the inference of any sort of negative ions other than the normal. The lower parts of Haines's curves could be interpreted to indicate nothing other than the gradual decay of the ephemeral free electrons. Even Haines himself was not quite definite, as he said, about the existence of that class of ions he designated by *C*.

Thus while it would not be in keeping with the spirit of modern experimental methodology to make any dogmatic statement regarding the existence or non-existence of these other kinds of negative ions in hydrogen, there seems to be in Haines's experiment no evidence of the existence of these other ions which he claimed to have discovered.

Aside from the fact that no indication of these ions could be found in the present experiment, and that there was no evidence inherent in Haines's results of their existence, there were positive experimental evidences against them. Franck¹ had found the mobility of the restatoms, namely the positively charged atoms of thorium D, in hydrogen, the same as that of the positive hydrogen ions. Now, as the molecular weight of hydrogen is 2 and that of thorium D is 208, it would follow, so reasoned Franck on the basis of the theory which led Haines to infer these other ions, that the positive hydrogen ion must consist of at least 20 hydrogen molecules in order to have the same mobility as the restatom. That being the case, the normal negative ion, according to the ratio given by Haines, must be a cluster of at least 14 molecules, and the supposed ions *B* and *C* must be constituted respectively by at least 7 and 2 molecules. Whether the number of molecules constituting the various species of ions be deduced from the results of Franck or from those of Haines, it would be expected that the ions would disintegrate when a high electric field was applied; only the disintegration would occur much sooner if the former were the case. Furthermore if disintegration did appear it would appear with the positive ions first, then with the normal negative ions, and then with the other; and if there were ions that were likely to remain intact it would be the ions designated by

¹ J. Franck, Ver. d. Deut. Phys. Ges., 11, 397, 1909. Also Franck u. J. Weitner, Ibid. 13, 671, 1911.

Haines as *C*. In other words, the positive and the normal negative ions would be the first to dissociate, and their dissociation would manifest itself in the disappearance of the inflections of the curves from which their normal mobilities were computed, and there would remain only the inflections indicating the mobilities of *C*—and possibly *B*. But as the results of the present experiment showed the positive and the negative mobilities to remain absolutely normal under the high field employed, whereas no indication of the higher mobilities could be found, it is evident that no combinations such as claimed by Haines ever existed and that each ion was a single charged molecule. If, on the other hand, Franck's conclusion that the mobilities of ions were independent of their masses¹ was accepted, then it would at once shatter the foundation upon which these various congregations of molecules called ions were built.

Thus it can be asserted with reasonable certainty that there existed in hydrogen no species of negative ions other than the one kind which was constituted by a single negatively charged molecule.

5. *Relative Amount of Free Electrons under High and Low Potential.*

As to the amount of free electrons found at high potential as compared with that found at low potential no absolute comparison could be made. Such comparison was rendered impossible by the difference between the time necessary for one and the other set of measurements. A set of measurements with the high-frequency high-potential oscillating field took from two and a half to three hours, whereas a set of measurements with the low-potential took only from forty-five minutes to an hour. Thus in the former case the rate of dissipation of the free electrons was great in comparison with the rate at which the measurements were made, and undoubtedly a large proportion of the free electrons had decayed before the measurements were completed. That this was the case may be seen from Figs. 4 and 5 where the slope of the lower part of the curves dropped considerably when the measurements were made a few hours later.

However, an approximate comparison may be made between the critical distances and potentials in the two cases by making proper allowance for the aging effect. Thus a comparison may be made between curve II., Fig. 3, and curve II., Fig. 4. In the case of the former the chamber was freshly filled just before the measurements were started; and the measurements represented by the point *A* were made about an hour and a half afterwards—that is, at the middle of the set. Curve II., Fig. 4, was taken three hours after the chamber was filled. Thus the

¹ J. Franck, loc. cit.

measurements represented by A in Fig. 3, and those represented by A' in Fig. 4, may be considered as taken when the gases in the two cases were approximately of the same state in so far as aging effect is concerned— A of course was reached an hour earlier. Now, at the point A the plate distance was 10 mm., the potential was 4,000 volts, and the pressure was 748 mm., while at the point A' the plate distance was 20 mm., the potential 56 volts, and the pressure 752 mm. If the amount of free electrons was the same in both cases A should have a much greater ordinate than A' . But just the reverse is shown by the curves. Thus it would be reasonable to conclude that at these points the amount of free electrons was less in one than in the other case. And since the aging effect, the only factor found thus far to have any influence upon the amount of free electrons present in the gas, was approximately the same in both cases, and since the only difference between the conditions under which the measurements were made was that of potential, it follows that the amount of free electrons present in the gas was smaller under high than under low potential.

This would seem to suggest that the electrons—some of them at least—did actually attach themselves to neutral molecules and thus form, when a high potential was applied, negative ions. This would not be at all impossible since the tremendous velocity imparted to them by the high electric field would enable them to produce ions from neutral molecules by attaching themselves to the latter at collision. It would be interesting to find out where, that is, at what potential—other conditions remaining the same—this sort of ionization actually would begin.

6. Summary of Results for Hydrogen.

The results of the mobility measurements for hydrogen are given in Table II. The annotations of the various columns are similar to those of Table I.

TABLE II.

Results Obtained from the Measurements on Hydrogen, May-June, 1917.

1. 14,758 cy. 4,000 volts.

$U+$.	$U-$.	$X+$.	$X-$.	P .	$K+$.	$K-$.	R .
5.51	8.20	6,669	5,668	748	5.43	8.10	1.49
5.92	8.20	6,669	5,668	748	5.81	8.10	1.38
5.51	8.20	6,669	5,668	746	5.40	8.10	1.49
8.20	12.21	5,668	4,723	518	5.58	8.35	1.49
14.94	20.99	4,192	3,524	290	5.70	8.15	1.41
14.94	20.99	4,192	3,524	300	5.84	8.35	1.41
Mean					5.56	8.19	1.45

2. 60 cy.

5.28		77.8		748	5.21		
5.50	8.80	25.0	16.5	746	5.41	8.65	1.52
6.60	11.19	20.0	13.0	600	5.22	8.80	1.62
8.95	13.28	29.5	24.0	498	5.85	8.70	1.48
13.90	22.00	19.8	11.5	300	5.49	8.69	1.58
22.91	31.06	16.5	9.0	198	5.95	8.15	1.34
....	9.26		28.0	746		9.26	
Mean					5.52	8.71	1.57
Mean of both frequencies					5.54	8.45	1.51

$X - /P$ Max. = 12.15, Min. = 0.38.
 $X + /P$ Max. = 14.45, Min. = 0.66.

It may be seen that with a potential gradient of 6,669 volt/cm., or $x/p = 14.45$, the positive mobility remained absolutely constant. The negative mobility remained constant with 5,668 volt/cm., and

Fig. 7.

Nitrogen. $P = 750$ mm.; $N = 14,758$ cycles; $E = 5,000$ volts.

$x/p = 12.15$. Thus it can be concluded that the law $Up = \text{constant}$ was verified for hydrogen up to these limits.

7. Nitrogen.

Fig. 7 shows the kind of curves obtained for nitrogen under the high-potential oscillating field. The negative curve here exhibited no exten-

sion and thus indicated the absence of free electrons during the measurements. As there were in the low-potential measurements indications of the presence of free electrons it seems highly probable that the complete disappearance of them under the high field was due to their forming negative ions with the neutral molecules.

The presence of an abundance of free electrons is indicated by the curves in Fig. 9, plotted from the measurements under 140 mm. pressure.

However, as it may be seen from Fig. 8, the amount of free electrons

Fig. 8.

Nitrogen. $P = 360$ mm.; $d = 1.0$ cm.; $N = 60$ cycles.

present in nitrogen was much smaller than that in hydrogen at the same pressure.

The aging effect here, as it was in the case of hydrogen, was to reduce the amount of free electrons. This might be due to the dissipation of the electrons into the wall of the chamber or to the presence of impurities which had crept in in the meantime.

Table III. shows a summary of results obtained for nitrogen. The maximum potential gradient employed was 17,670 volt/cm., for the positive, and 14,880 volt/cm., for the negative ions. The mobilities remained absolutely normal up to these limits and the law $Up = \text{constant}$ is applicable here as it was in the case of air and hydrogen.

Fig. 9.

Nitrogen. $P = 140$ mm.; $d = 2.0$ cm.; $N = 60$ cycles.

TABLE III.

Results Obtained for Nitrogen, July, 1917.

1. 60 cy.

$U+$.	$U-$.	$X+$.	$X-$.	P .	$K+$.	$K-$.	R .
17.60	22.96	15.0	11.5	60	1.39	1.81	1.30
....	10.15		26.0	140		1.87	
2.81	3.88	47.0	33.5	360	1.33	1.84	1.38
1.27	1.65	51.0	40.0	750	1.26	1.62	1.30
1.36	1.84	50.0	38.0	745	1.33	1.80	1.35
1.34	1.82	49.8	38.0	745	1.31	1.78	1.36
Mean.....					1.32	1.79	1.34

2. 14,758 cy. 5,000 volts.

1.31	1.84	17,670	14,880	750	1.29	1.82	1.40
1.31	1.84	17,670	14,880	745	1.28	1.80	1.40
1.31	1.84	17,670	14,880	742	1.28	1.80	1.40
2.76	3.93	13,910	10,110	360	1.31	1.86	1.42
2.76	3.93	13,910	10,110	345	1.26	1.78	1.42
Mean.....					1.28	1.81	1.41
Mean of both frequencies.....					1.30	1.80	1.38

$X - /P$ Max. = 29.0, Min. = 0.05.
 $X + /P$ Max. = 40.0, Min. = 0.07.

CONCLUSION AND DISCUSSION.

As no indication was exhibited by the results of the present experiment of the breaking down of the law $Up = \text{constant}$, it must be concluded therefrom that both the positive and the negative ions did not disintegrate at the potentials employed.

It has been indicated elsewhere in this paper that the cluster hypothesis demands the disintegration of the ions when the potential gradient X , or the ratio X/p (where p is the pressure in mm. mercury) is sufficiently high. According to Townsend¹ the disintegration should commence when X/p is about 0.1. In the present experiment the potential gradients applied were 14,160, 6,669, and 17,670 volt/cm., respectively, for air, hydrogen, and nitrogen, when the positive mobilities were measured. The values of X/p here ranged from 0.22 to 22.04 for air, 0.66 to 14.45 for hydrogen, and 0.07 to 40.0 for nitrogen. The negative mobilities were measured at potential gradients as high as 12,870, 5,668, and 14,880 volt/cm., for the gases in the order named. The values of X/p here ranged from 0.18 to 20.70 for air, 0.38 to 12.15 for hydrogen, and 0.05 to 29.0 for nitrogen. As the results show no tendency on the part of either the positive or the negative ions to disintegrate under these conditions they must be interpreted as contradictory to the hypothesis.

On the contrary, these results are in perfect agreement with the atom-ion hypothesis. Taking this in conjunction with the results of other experiments, especially those of Wellisch and Loeb, there does not seem to be any doubt at all regarding the validity of this hypothesis; and the cluster hypothesis must resort to other than the usual arguments for its support.

There is left an experimental fact which the cluster hypothesis may conceivably rely upon for support, and that is the difference between the positive and negative mobilities found by actual measurements. On the basis of the cluster hypothesis the relatively smaller mobility of the positive ion is attributed to its greater size as compared with the negative ion. It is argued that if both the positive and the negative ions are single-charged molecules why should they have different mobilities when their charges and sizes are the same? The difference between the positive and the negative mobilities therefore must be conceived as due to the difference between the sizes of the two kinds of ions. The positive mobility being smaller, the positive ion must therefore be heavier. This appears quite plausible at first sight; and it does seem, indeed, as though no such reasonable explanation could be offered by the exponents of the small ion.

¹ Townsend, *Electricity in Gases*, Oxford, 1915.

This difficulty of the small-ion hypothesis, however, is more apparent than real. For, in view of recent theories as to the electronic constitution of matter it would not be reasonable for the exponents of the small ion to expect equality between the two kinds of mobilities. The ordinary theoretical derivation of the formulæ for mobilities, it should be remembered, involved a fundamental presupposition that the mean free path is the same for the positive as for the negative ions. That this assumption is unjustifiable will be seen from the following considerations.

If an atom is formed by a positive nucleus surrounded by a system of negative electrons held together by attractive force from the nucleus,¹ the phenomenon of ordinary molecular collision must be attributed to the repulsion between the two systems of negative electrons on the colliding molecules. "The reason that two molecules thus rebound from one another when in their motion of thermal agitation their centers of gravity approach to a distance of about 2×10^{-8} cm., is presumably that the atom is a system with negative electrons in its outer regions. *When these negative electrons in two different systems which are coming into collision approach to about this distance, the repulsions between these similarly charged bodies begin to be felt, although at a distance the atoms are forceless. With decreasing distance this repulsion increases very rapidly until it becomes so great as to overcome the inertias of the system and drive them asunder.*"²

There does not seem to be any reason why the above conception may not be extended to the case of a collision between an ion, which is a charged molecule, and a neutral molecule. When the ions approach the neutral molecules the negative electrons in the two systems are brought close to each other and the force of repulsion between these peripheral electrons will begin to manifest itself.

Thus between an ion and a neutral molecule there exists, besides the attraction due to the charge in the ion, a repulsion due to the peripheral negative electrons. These two forces would effect the mean free path of the ions in opposite direction—the former causing it to decrease while the latter cause it to increase—and the *effective mean free path* would depend on their algebraic sum.

Furthermore, if the process of positive ionization consists in the detachment of a single negative electron from a neutral molecule, and that of negative ionization consists in the attachment of a negative electron to a neutral molecule, it should be expected that the repulsive forces would be different when the two kinds of ions collide with a molecule which is

¹ Rutherford, Phil. Mag., XXI., 669, 1911.

² Millikan, The Electron, 181, 1917. Italics mine.

not charged. The repulsion between a negative ion and a neutral molecule would be greater than that between a positive ion and a neutral molecule, since there are more negative electrons in the negative ions than in the positive.

Thus, assuming that the attraction between the positive ion and the neutral molecule is the same as that between the negative ion and the neutral molecule—and there is every reason to suppose this to be the case—we should expect the *effective mean free path* to be greater for the negative ion than for the positive. And since the mobility is proportional to the *effective mean free path* the negative mobility would be greater than the positive.

An illuminating example of this may be derived from the Bohr atom¹ which is an embodiment of the nucleus atom. As we are here primarily interested in the molecule we may take as example the Bohr hydrogen molecule,² which is the simplest treated. A hydrogen molecule here is conceived of as a system of two positive nuclei situated at a distance $2b$ apart with two negative electrons travelling in a circle of radius a in the plane perpendicular to and bisecting the axis joining the nuclei. Extending this conception to the hydrogen ions, we have the positive ion consisting of a single negative electron, and a negative ion of three negative electrons, all circling about an axis joining two positive nuclei. Thus the number of negative electrons in the colliding systems would be 5 in the case of a collision between a negative ion and a neutral molecule, and 3 in that of a collision between a positive ion and a neutral molecule. The ratio of the negative to the positive mobilities must somehow vary with the ratio of 5 to 3—although the writer is not prepared at present to say what sort of proportionality there exists between the two quantities.

From this point of view we may expect the ratio of the negative to the positive mobility to approach unity as the total number of negative electrons in both the ions and the neutral molecules increases. For, as the difference between the total number of negative electrons in a positive ion colliding with a molecule and that in a negative ion colliding with a molecule is always two, it can easily be seen that this difference would not result in an appreciable difference in the ratio between the two numbers when they are sufficiently large. This is what has actually been found in the cases of gases the molecules of which are of a more complex structure. The positive mobility is found in these gases to approach the negative.

¹ Bohr, Phil. Mag., XXVI., 1913, pp. 1, 476 and 857; XXIX., 1915, p. 332; XXX., 1915, p. 394.

² Phil. Mag., XXVI., 1913, p. 863.

Furthermore, as the repulsive force varies inversely with the distance between the colliding systems it follows that the more peripheral the negative electrons are the smaller this force would be. And hence with charged and uncharged molecules of gases of more complex structure the repulsive forces would be very nearly the same whether the ion contains one more or one less negative electron than the uncharged molecule. Thus we should expect the two kinds of mobilities to approach each other in the cases where the gases are of a more complex nature.

But the above explanation for the differences between positive and negative mobilities would not be applicable to the cases where the ratio of the negative to the positive is less than unity. This would be a real stumbling block indeed if the mobilities in such cases had been accurately determined and the differences found between them had been sufficiently great. As far as evidences are available the differences between the positive and negative mobilities are, when the former are greater, never more than a few per cent., which may very well be due to experimental fluctuations.

However, an experiment is now in progress to redetermine the mobilities of some of the gases in which the positive had been found to be greater than the negative, and until conclusive evidence resulted in the actual establishment of real differences which cannot be attributed to experimental fluctuations, the above explanation seems to be the most reasonable one so far advanced.

SUMMARY.

To reiterate then:

1. The previous experiment of Loeb on the ionic mobilities in air has been repeated and confirmed.
2. The law $Up = \text{constant}$ was found to hold for the negative ions from 134 to 12,870 volt/cm. or from $X/p = 0.18$ to 20.70; and, for positive ions from 186 to 14,160 volt/cm., or from $X/p = 0.22$ to 22.04.
3. The experiment was extended to hydrogen and nitrogen, and the law $Up = \text{constant}$ was found to hold in both cases.
4. The law $Up = \text{const.}$ was verified in hydrogen for negative ions from 9 to 5,668 volt/cm. or from $X/p = 0.38$ to 12.15; and for positive from 16 to 6,669 volt/cm. or from $X/p = 0.66$ to 14.45.
5. In nitrogen, negative mobility was found to remain constant from 11 to 14,880 volt/cm. or from $X/p = 0.05$ to 29.0; and the positive mobility constant from 15 to 17,670 volt/cm., or from $X/p = 0.07$ to 40.0.
6. Free electrons were found to exist in both hydrogen and nitrogen even at atmospheric pressure; more in hydrogen than in nitrogen.
7. More free electrons were found with low potentials than with high potentials.

8. The aging effect upon the gases at constant pressure was to reduce the relative amount of the free electrons.

9. No indication was found of Haines's negative ions *B* and *C* and in general no indication was found so far which would prove to be favorable to the cluster theory.

10. The difference between positive and negative mobilities are explained by the nucleus-atom theory, and an experiment is now in progress with the gases where the proposed explanation does not seem to be applicable.

In conclusion the writer wishes to register his appreciation and gratitude to Professor R. A. Millikan for the kind encouragement and direction he received during the present experiment. He also wishes to thank Dr. A. J. Dempster, to whose enthusiasm and experience he resorted during Professor Millikan's temporary absence from Ryerson Laboratory. And finally he wishes to express his appreciation for his initiation into the technique of the experiment by Dr. Leonard B. Loeb, his friend and former colleague.

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