THE FORMATION OF NEGATIVE IONS IN AIR.

By Leonard B. Loeb.

Synopsis.

Mobility of Negative Ions in Air at Low Pressures.—The purpose of the experiments was to decide between the two theories of the formation of negative ions, proposed by Wellisch and by J. J. Thomson. The carriers were generated as photo-electrons by focusing ultra-violet light on one plate of a condenser at grazing incidence, thus eliminating stray light effects. Great care was used to secure pure air. The *curves* obtained agree in general with the results of previous investigators; they show anomalous mobilities below a critical pressure which was found to vary with the frequency of commutation of the E.M.F. No "free electrons" of the Wellisch type were observed. A repetition of the Wellisch experiments with photo-electrons showed that the "free electrons" were really a type of carrier which, started as electrons but attached themselves to molecules in the measuring field, as the Thomson theory demands. To *test the Thomson theory*, curves were computed assuming certain values for the constants. Theoretical and observed curves are similar in shape; in particular, the inflections near the low voltage end fall fairly closely together; It is also shown that the Wellisch *results* are in accord with this theory. The *chance of negative ion formation constant*, $1/n$, comes out about $1/2.5 \times 10^5$ *for air*. As $1/n$ is 0 for *nitrogen*, and as $1/n$ in *oxygen* is about 1/50,000, we conclude that it is to the oxygen molecule in air that electrons attach to form ions.

Introduction.

It has long been known that the velocity in unit electric field (*i.e.*, mobility) of normal negative ions in air ceased to be strictly inversely proportional to the pressure, for pressures below 10 cm. of air. In fact for pressures lower than this the mobility has been found to increase more rapidly than the pressure decreased. This behavior has been taken as powerful evidence for the existence of so-called "cluster" ions, but the work of Wellisch (1), Loeb (2), and Yen (3) has shown that the assumption of a fairly stable cluster ion must be given up. One must accordingly look elsewhere for an explanation of the foregoing phenomenon.

In most if not in all ionization processes in gases the first step consists in the liberation of an electron from a neutral atom or molecule. As all evidence points to the fact that the normal negative ion in a gas is a body of molecular dimensions, the electrons formed by the ionizing agent must first attach themselves to neutral gas molecules in order to form the type of carriers that are usually observed. It seems quite likely that in this process may lie the explanation of the abnormal mobilities of gas ions observed in air at low pressures.

In fact Sir J. J. Thomson (4) proposed a theory to account for these abnormal, or better "anomalous," mobilities, on the basis of a definite mode of formation of ions from electrons and neutral molecules. This theory assumes that out of n collisions of an electron with a given type of neutral molecule on the average only one will result in the attachment of the electron to the molecule: n being a constant characteristic of the type of gas molecules considered. Such an assumption might be interpreted as meaning that a certain region of the molecule must be struck by the electron under the proper conditions (*e.g.*, such as the velocity of the electron or the state of the molecule) before it can be incorporated in the molecule. It is obvious that if n be great enough, particularly at low pressures, the electron might cover considerable distances as an electron before attaching itself to a molecule to form an ion. Thus since the mobility of the electron is of the order of a hundred fold that of the ion it would be expected that below certain pressures the mobility of the negative ions would show abnormalities. On the basis of this theory J. J. Thomson derived the equations governing the behavior of carriers which change their nature while being measured as a function of the pressure. His computations are applicable to the Langevin method of mobility determination.

In two very able papers Wellisch (1) published the results of an investigation of the mobilities of positive and negative ions at low pressures in air as determined by the Franck (5) modification of the Rutherford alternating current method. Down to 8 cm. he observed the single class of carriers of slightly abnormal mobilities observed by the earlier workers (5). Below 8 cm. pressure his curves were of such a form that it seemed only possible to explain them on the basis of the existence of *two types of carriers*. These Wellisch interpreted as being carriers of mobilities approaching electronic magnitudes, which he termed "free electrons," and normal ions whose mobility was inversely proportional to the pressure down to about .15 mm. The interpretation of the process of ion formation given by Wellisch, as a result of his experiments (which yielded two types of carriers at pressures where other observers had found but a single type), differs radically from that offered by Thomson. Assuming that in air the carriers are of two distinct kinds, "free electrons" and ions, the former increasing in numbers relatively to the latter as the pressure decreases, Wellisch proposed the following theory. In order that an electron may attach to a molecule to form a negative ion he assumed that the electron must strike the molecule with a relative velocity, corresponding to a certain energy-value greater than E, which he styles the "potential energy of ion formation." If the energy at impact is greater than E the electron and molecule will unite to form an ion. If the energy of the impact be less than E the electron can never attach to the molecule. It then becomes a "free electron," which it remains unless it can acquire the energy E in the electric field. Now this energy E he further assumes is generally acquired in the act of ionization. In receding from the positive remainder of the molecule from which it came the electron transfers some of its initial kinetic energy to potential energy of separation. Accordingly if before striking its first molecule it has traveled so far that its residual energy is less than E it will remain a "free electron." The number of electrons which have a chance of thus remaining free will obviously be the greater the lower the pressure, for the mean free path of an electron is inversely proportional to the pressure.[1]

One has therefore two widely different theories of ion formation. The theory of Thomson assumes that out of a great many collisions the electron may strike a molecule in such a manner that it can attach, an event which if one is given enough impacts must eventually take place *for all electrons*. The theory of Wellisch postulates that it is the first impact that determines whether an electron shall form an ion or whether it shall pursue its subsequent career as a *permanently* "free electron." These theories represent different interpretations of the results of two slightly different methods of experimentation, which find reconciliation in the light of the results which follow.

The Problem.

In studying this question it became evident to the writer that no decision as to the validity of the two theories could be made without a further experimental investigation. Accordingly in October, 1919, a series of experiments were undertaken in order to attempt to solve this problem. What was needed was a method of distinguishing sharply between electrons and ions in experiments of the type of the earlier investigators. It was thought possible so to modify the general method used by Kovarik (6) as to make it serve this purpose. Kovarik measured the mobilities of carriers produced by photo electrons generated at the surface of a plate by light incident normally upon it, for various pressures in air, using the Rutherford alternating current method. In again taking up experiments of this sort an attempt was made to fulfil the following conditions.

[1] It is to be remembered that the force between the parent atom and the electron escaping from it is inversely proportional to the square of the distance and not to a relatively high power of the distance as in cohesion.

1. To use a detecting system having a high sensibility in order to detect the presence of small numbers of free electrons.

2. To use carriers all starting from the same plane as electrons.

3. To use fields as uniform as possible.

4. To control the upper limit of the velocity of emission of the photo-electrons, by filters if necessary.

5. To eliminate the effect of "stray light" which Kovarik claims to have been bothered by.

6. To eliminate all *organic vapors* and *impurities*.

7. To use a constant source of ultra-violet light.

Apparatus.

The apparatus finally evolved is indicated in Fig. 1. In an all metal case C are housed the two condenser plates P and E of 10 cm. diameter.

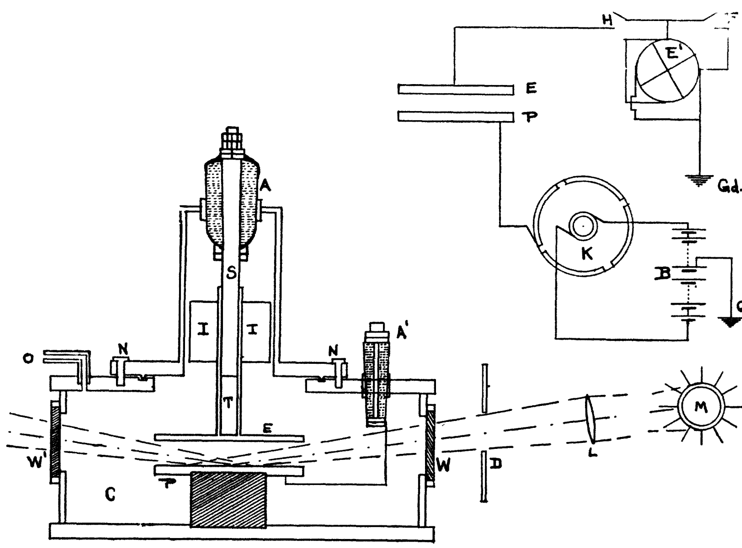

Fig. 1.

P was a plate of highly polished speculum metal which seemed to have quite suitable qualities as a constant source of photo-electrons. E was a plate of oxidized copper suspended by means of the threaded tube T so as to be approximately parallel to P. E could be screwed up or down on the threaded support S, by means of an electromagnet operated from outside the housing which acted on the iron mass I attached to T. S was insulated by an amber plug A ground into the top of the housing case C, and was attached to the electrometer system. The image of a quartz mercury arc M was focused upon P through a quartz window W, 4.5 cm.

in diameter, by means of the quartz lens L. From P most of the light was reflected out through a glass window W through which also the distance PE could be accurately measured by means of a cathetometer. The interior of C was oxidized so that the stray light falling on the walls of the housing emitted practically no electrons. The beam of light was still further cut down by the diaphragms D. Access into C was gained through the removal of the top of the case C, by unscrewing the screws N, which insured the tightness of the joint. This joint was made gas tight through the use of an unvulcanized rubber gasket, similar to those used by Professor Millikan in the attainment of high vacuua on his vacuum spectrometer.

In sealing in the windows of the chamber C as well as in securing gas tight joints at the amber insulating plug A^1, which carried the leads from the plate P to the source of the alternating current, great care was taken to make the possibility of the diffusion of any vapors from these points into the case negligible.

The electrometer E^1 was one of the Dolezalek type having with its system of switches and leads an electrostatic capacity of 260 E.S.U. and a sensibility of 3,700 mm. per volt on a scale 2 m. distant. The alternating potential came from a bank of dry cells B the center of which was grounded at Gd, the other poles of which were connected to the two brushes of a commutator K. Two commutators were used, one having twenty segments, and the other one having two segments. They were driven by a motor through sets of gears having the ratios 5 : 1, 2 : 1, and 1 : 1. The speed of the motor was 2,100 R.P.M. so that by changing gears and commutators a fairly complete control of frequency of alternation lying between 15 and 750 cycles per second was obtained. The speed of the commutator was measured directly by means of a revolution-counter and stopwatch. The speed was kept constant by regulating the field current of the motor. Small variations in the speed of the motor were registered by variations in the E.M.F. given by a small dynamo driven by the shaft of the driving motor. This indicator was so sensitive that any desired degree of constancy could be obtained.

The air used in the measurements was purified in the following manner. It passed through a tube of copper oxide heated to dull redness to destroy any organic vapors present. The air then passed through long tubes of $NaOH$, $CaCl_2$, and P_2O_5, finally passing through a trap cooled to from $-125°$ to $-90°$ C. by frozen alcohol. Before any series of measurements on air was made, the apparatus was exhausted to about 2 cm. and filled to atmospheric pressure with the purified air at least three times, generally more.

THE MEASUREMENTS.

Measurements were conducted for a given pressure and a given frequency of commutation by determining the variation of the current to the electrometer plate as a function of the value of the alternating potential applied to P. This was accomplished by disconnecting the lead to the electrometer at switch H, leaving the latter grounded through F and allowing the alternating potential to act on plate P for a given time (from 5 to 30 seconds). The electrometer ground F was then disconnected, the plate E connected to the electrometer, and the deflection noted. Since the capacity of the leads to the electrometer was appreciable compared with the capacity of the condenser formed by the plates P and E, a correction of about 7.5 per cent. had to be subtracted from the value of the P.D. given by the commutator, in order to give the true value of the P.D. acting across P and E.[1] In general the potentials taken from the cells were so arranged that the value of the positive or retarding, potential applied to the plate P by the commutator, was always from 2 to 20 per cent. higher than the corresponding negative, or accelerating potential. The purpose of this was to prevent any possibility of carriers *working* their way across from P to E by stages covering several cycles. Control experiments showed that the magnitude of this difference in the two sides of the alternating P.D. did not play any rôle as long as the retarding potential was a trifle greater than the accelerating potential. The values of the deflections for various potentials were generally taken starting at the higher values and going down to the lowest, then working back again over the curve taking values of the potentials at intermediate points between those first chosen. The readings were always quite consistent, unless by some accident the value of the potential across the mercury arc had changed during the measurement. For a series of readings on a given sample of air the curve at atmospheric pressure would be taken first, and then the values for the lower pressures were obtained, the pressure being reduced step by step, by means of a water aspirator. The range of pressures over which satisfactory work could be done in air, lay between 760 mm. and 30 mm. Below this pressure it was impossible to go because the frequencies attainable by the commutator were not high enough for the type of curves obtained. The frequencies used varied from 15 cycles per second to 750 cycles while the distances between P and E varied

[1] The total fall of potential given by the commutator was distributed across the condenser formed by P and E, and the condenser formed by the leads and the ground, these two representing condensers coupled in series. The true field acting on the carriers was then less than that produced by the commutator. Measurements made by the method of mixtures gave this correction as 7.5 per cent.

from 1 cm. to 1.7 cm. At some point in each series of determinations, for a given sample of air a "control" set of readings was taken in which the deflection of the electrometer was measured when different steady negative potentials were applied to the plate P, for a given time. This gave the saturation photo-electric current from the plate P under the influence of the arc at the time of experiment. Knowledge of this current served as a means of comparing data taken on successive days. It was also of use in applying the theory of Thomson.

When the electrometer deflections for a given series of accelerating potentials were plotted against the value of the accelerating potential, curves of the type shown in Fig. 2, curves I., II., III., IV., and V., were

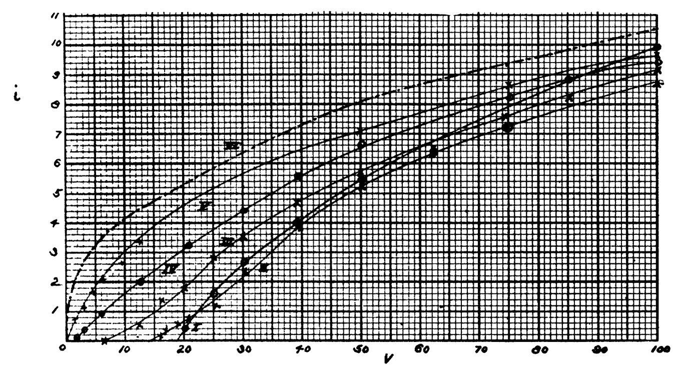

Fig. 2.

June 2, 1920. d = 1.05. Electrometer deflections in cm. scale reading plotted against the alternating P.D. on P.

I.	p = 747.0	N = 35.7	Mobility K' = 2.27
II.	p = 98.0	N = 359.0	" K' = 2.97
III.	p = 75.5	N = 705.0	" K' = 7.92
IV.	p = 53.5	N = 705.0	" K' = 26.0
V.	p = 38.5	N = 705.0	" K' = 39.4
		Observed x. . . x. . .	
VI.		Saturation —. —. —.	

obtained. These correspond to different pressures and to different speeds of commutation. The curve numbered VI. in the figure is the control or saturation curve taken with a series of steady negative potentials applied to plate P. The curves in general have the characteristic form of mobility curves. They are nearly parallel to the saturation curves at the higher potentials, and then drop sharply towards the potential axis tending to cut it at some fairly well defined point. The voltage value of this point one may designate as V_0. In the curves obtained at the higher pressures this point is quite sharply defined.

If the value of V_0, obtained from a given curve and corrected for the potential drop across the electrometer leads by being reduced by 7.5 per cent. of its value, be inserted as V_0 in the equation $U = Nd^2/V_0$ (where N is the frequency of commutation in half cycles, and d is the distance between the plates), the average value of U the mobility of the carriers between the plates is obtained. If the U thus obtained for a given pressure, be multiplied by the factor $p/760$ (where p is the pressure in mm.), the value of K the *mobility constant* for normal ions in air should be obtained. The values of K for the curves depicted in Fig. 2 may be computed from the data given in the legend. They are 2.27, 2.97, 7.92, 26 and 39.4. cm. per second respectively for curves I., II., III., IV. and V., Fig. 2.

Results.

The results of twenty-five different series of determinations, taken under all imaginable conditions in air, may be summed up as follows:

1. No evidence of the existence of the *two* types of carriers described by Wellisch could be found in these results, although they were carefully looked for; nor was there any evidence of the "free electrons" of Wellisch. Such carriers would have been indicated by complex curves of the types shown in Figs. 14 and 15, taken under different circumstances.

2. The curves were consistently of the types shown in Fig. 2 having intercepts with the voltage axis V_0 which above 100 mm. pressure yielded approximately normal values of K. The values of V_0 obtained at pressures below this gave anomalous values for K which were in general accord with the values found by Kovarik.

3. The value of K for carriers below 100 mm. pressure was found to be a conspicuous function of the frequency of commutation. This is again in agreement with the experimental results of Kovarik.

4. The anomalous values of K for air were not always the same under similar conditions but varied somewhat with the purification which the air had undergone.

5. As may be seen in the figures, the apparently sharp intercepts of the curves with the potential axis begin to vanish below about 100 mm. and the feet of the curves tend to approach the axis more and more asymptotically the lower the pressure (see especially II. and III.). The appearance of such feet in the curves was also noted by Kovarik who ascribed them to "stray light" effects. A careful study of these portions of the curves which appear in all curves when the pressures become low enough, under all conditions of illumination and plate distance, is sufficient to show that *they are intimately connected with the phenomenon of the anomalous mobilities and are not due to stray light.*

It may be concluded from the above summary that these results verify the experimental results of the early observers. They however go a step further than those results indefinitely connecting the asymptotic portions of the curves near the potential axis with the phenomenon of the anomalous mobility. The work was carried out in such a manner that it permits an attempt at the quantitative application of the results to the theory of J. J. Thomson.

Application of Results to Thomson Theory.

For carriers liberated at one plate P of a parallel plate condenser, and accelerated for a time T to the other plate E distant d, by a potential difference of value V only those carriers will reach E which have for a velocity in unit field a value U given by

(1) $$U \geqq d^2/VT(1).$$

Now the theory of J. J. Thomson assumes that an electron starting from P and moving towards E in the electric field may on its career in one out of n impacts collide with a gas molecule in such a manner as to attach itself to the molecule, and thus continue its way to E as an ion. A carrier which reached E after undergoing such a change must have had an average, "hybrid" mobility U which is determined by the condition laid down above. The value of U for such a carrier would then lie between that of an electron and that of an ion. In other words it would have a "fictitious" abnormal or an anomalous mobility such as is observed for carriers in air at pressures below 100 mm. Assume that such a carrier travels x cm. as an electron and $(d - x)$ cm. as an ion. If K' be the mobility of an electron and K be that of an ion the time T taken to travel d in unit field will be

$$T = x/K' + (d - x)/K.$$

Since however K' is of the order of 100 times as great as K, one may for all practical purposes neglect the first term and write

$$T = (d - x)/K.$$

Since $U = d/T$ one may write

$$U = \frac{Kd}{(d - x)},$$

which expresses the fictitious hybrid mobility, in terms of the mobility of the ion and the ratio of the whole distance to the distance traversed as an ion. In order to get a current from P to E with an alternating current whose time of alternation is T one must impose the condition (1), which gives:

$$U = K\frac{d}{(d - x)} \geqq d^2/VT.$$

This implies that in order to reach E at all the carrier must have covered a distance x as an electron, x being governed by the equation

$$d - KVT/d \leqq x. \tag{2}$$

This condition can only hold up to $(KVT)/d = d$, for negative values of x have no meaning.

On the basis of the assumptions quoted, and further assuming that *the velocity of drift of the electrons in the electric field is small compared to their velocity of kinetic agitation*, Thomson shows that out of I_0 electrons starting from P the number I which go a distance x without uniting to form ions, is given by the equation

$$I = I_0 e^{-Wx/(nK'\lambda V/d)} \tag{3}$$

(where W is the mean velocity of kinetic agitation of the electrons, d the distance between the plates, K' the mobility of the electron, λ the mean free path of the electron, and $1/n$ the chance that any collision of an electron with a molecule will result in the formation of an ion). Now the carriers that have traveled a distance x without combining to form an ion can only be detected when they contribute to the current from P to E, so that in order that the above equation (3) may apply to the carriers detected, one must include the condition imposed by (2), viz., that

$$x = d - KVT/d,$$

where x can have only positive values. Putting this condition into (3) one obtains

$$I/I_0 = e^{\frac{-dW}{nK'V\lambda}(d - KVT/d)}. \tag{4}$$

Which gives the fraction of the initial electron current starting from P that reaches the plate E as a function of the experimental variables d, V and T. Furthermore since K is inversely proportional to the pressure, and assuming K' and λ to be so (*i.e.*, to be proportional to $760/p$, where p is the pressure in mm. at which the measurements are made), and finally writing $T = 1/N$ the equation (4) becomes

$$I/I_0 = e^{\frac{-W}{nK'\lambda}\left(\frac{d^2(p/760)^2}{V} - \frac{K(p/760)}{N}\right)}. \tag{5}$$

If one assumes that the electrons are in thermal equilibrium with the gas molecules he may evaluate W. Taking λ for the electrons as $4\sqrt{2}$ times that of the molecules, and assuming that K' for electrons is about 200 (1, 7) while K for ions is about 2, the equation becomes applicable to experimental verification and the determination of the constant n, namely it takes the form

$$I/I_0 = e^{\frac{-9.9 \times 10^8}{n}\left(\frac{d^2(7/760)^2}{V} - \frac{(2p/760)}{N}\right)}. \tag{6}$$

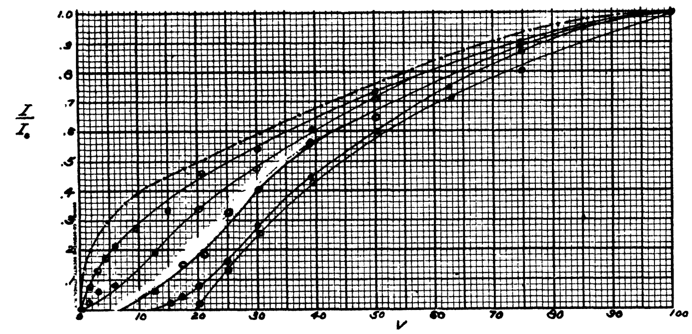

Fig. 3.

June 2, 1920. $d = 1.05$. Curves of Fig. 2 reduced to fraction of saturation.

I. $p = 747.0$ $N = 35.7$
II. $p = 98.0$ $N = 359.0$
III. $p = 75.5$ $N = 705.0$
IV. $p = 53.5$ $N = 705.0$
V. $p = 38.5$ $N = 705.0$
Observed x. . . x. . .
VI. Saturation —. —. —.

On the basis of the experimental curves obtained one may solve for n from any curve by taking the values of I/I_0,[1] d, p, V and N under which the curve was determined, and substituting them in the equation above.

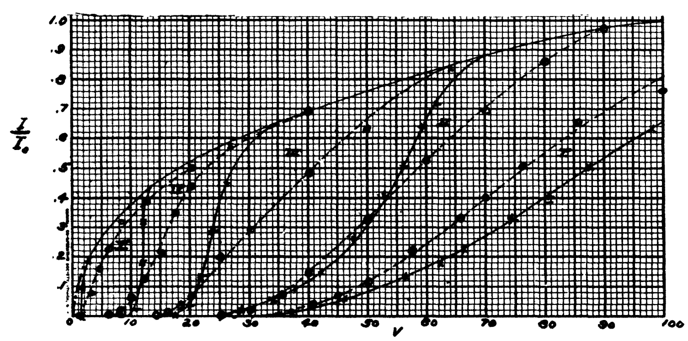

Fig. 4.

April 23, 1920. $d = 1.66$, $K = 2.1$, $p = 95$, $n = 2.5 \times 10^5$.

I. $N = 710$ III. $N = 362$
II. $N = 147$ IV. $N = 72$
V. $N = 14.7$
Observed o. . . o. . .
Computed –x———x–
Saturation —. —. —.

[1] I/I_0 was taken as the ratio of the electrometer deflection at a given voltage V taken with alternating potentials to the deflection obtained by letting the same steady voltage act for half the time. This gives the ratio of the true I/I_0 corrected for the decrease in the saturation current at the lower potentials.

In doing this it was found advisable to take points on the curves lying near the feet (*i.e.*, at values of V near those giving the abnormal mobilities for the curves). The reason for this will become evident later on. Solu-

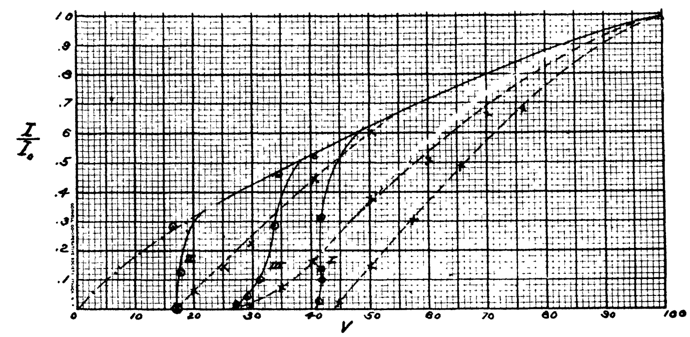

Fig. 5.

April 27, 1920. $d = 1.66$, $K = 2.45$, $n = 2.5 \times 10^5$.

I. $p = 738$ $N = 37.2$
II. $p = 738$ $N = 15.2$
III. $p = 148$ $N = 150.0$
Observed x. . . x. . .
Computed –o———o–
Saturation –. –. –. –.

tions of this equation for some fifteen or more different curves were made at one time or another. The curves so studied covered a range of pressures from 130 mm. down to 20 mm. in pressure, and frequencies ranging

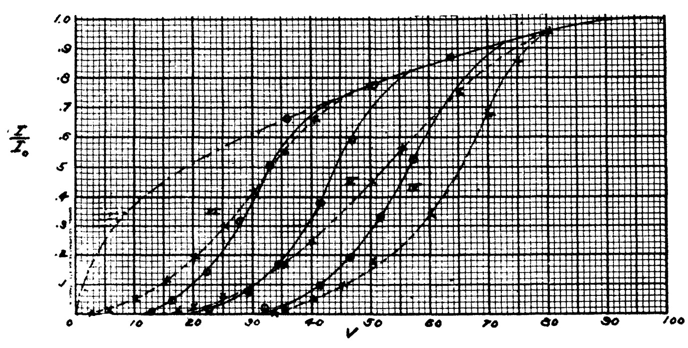

Fig. 6.

April 27, 1920. $d = 1.66$, $K = 2.45$, $n = 2.50 \times 10^5$.

IV. $p = 105$ $N = 372$
V. $p = 84$ $N = 378$
VI. $p = 59.2$ $N = 378$
Observed x. . . . x. . .
Computed –o———o–
Saturation –. –. –. –

from 150 cycles to 750 cycles. The determinations also utilized three different values of d ranging from 1.05 cm. to 1.66 cm. and were taken on at least five different samples of air purified under somewhat different

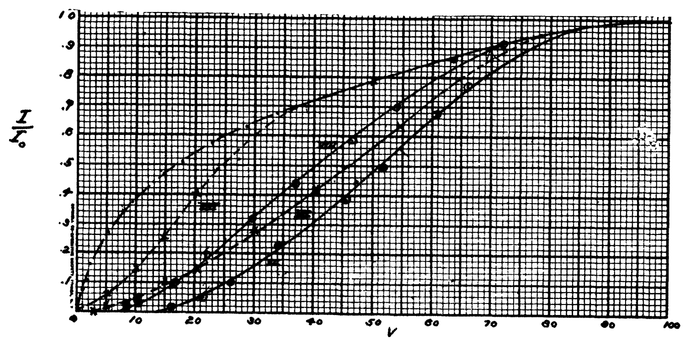

Fig. 7.

April 27, 1920. $d = 1.66$, $K = 2.45$, $n = 2.5 \times 10^5$.
VII. $p = 59.2$ $N = 742$
VIII. $p = 41.5$ $N = 742$
Observed x...x...
Computed -o———o-
Saturation —. —. —.

conditions. The values of n for air thus obtained ranged from 9×10^5 to 1.5×10^5, the greater portion of the values lying around 2.5×10^5. The reason for this variation will be considered in connection with a study of the curves. Measurements were made in pure oxygen, and in

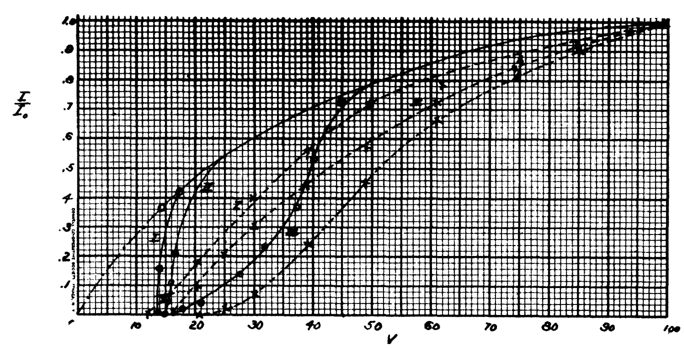

Fig. 8.

June 24, 1920. $d = 1.50$, $K = 2.55$, $n = 4 \times 10^5$.
I. $p = 752$ $N = 14.9$
II. $p = 198.5$ $N = 73.0$
III. $p = 99.5$ $N = 373.0$
Observed x...x...
Computed -o———o-
Saturation —. —. —. —.

nitrogen containing small percentages of oxygen, and will form the basis of a later paper. They covered pressures ranging from 760 mm. pressure to 15 mm. as well as frequencies from 37 cycles to 750 cycles and yielded

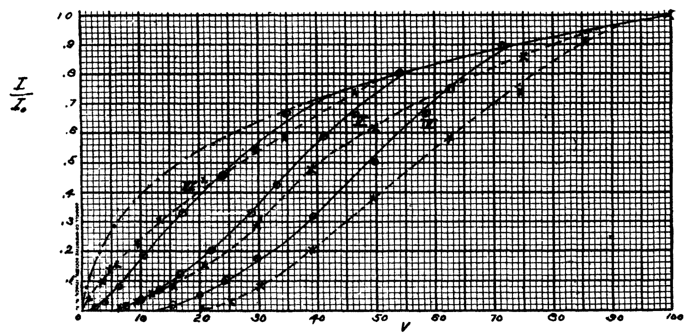

Fig. 9.

June 24, 1920, $d = 1.50$, $K = 2.55$, $n = 4 \times 10^6$.
IV. $p = 80.5$ $N = 727$
V. $p = 59.5$ $N = 740$
VII. $p = 32.5$ $N = 735$
Observed x. . . x. . .
Computed –o———o–
Saturation —. —. —. —.

values of n for air, computed back to air on the basis of the oxygen content, which agreed well with those already cited.

Using values of $n = 2.5 \times 10^5$ and 4×10^5 and using values of K, the ionic mobility, as calculated from the curve taken at 760 mm. (which

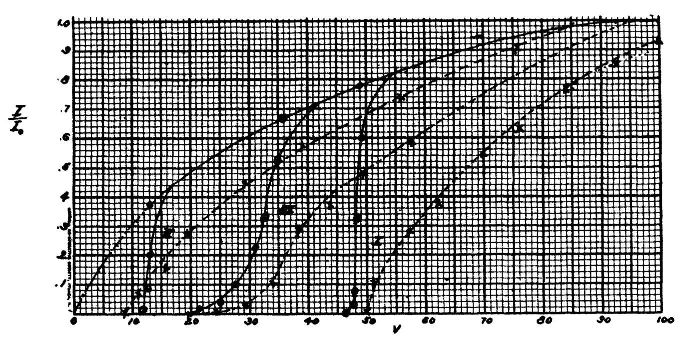

Fig. 10.

April 6, 1920. $d = 1.66$, $K = 2.16$, $n = 4 \times 10^6$.
I. $p = 744$ $N = 37.2$
II. $p = 207$ $N = 37.7$
III. $p = 134$ $N = 151.0$
Observed x. . . x. . .
Computed –o———o–
Saturation —. —. —. —.

ranged from 2.55 to 2.16 cm./sec.) the values of I/I_0 were computed as a function of V from the equation (6) for pressures and values of N under which some of the experimental determinations were made. The values of I/I_0 plotted as ordinates against the voltage V as abscissæ yielded a series of curves. These computed curves when corrected for the value of the saturation photo-electric current, and for the value of the reduction of potential between the plates due to the induction effect, are reproduced in Figs. 4 to 12 as full curves with circles. In the same figures are

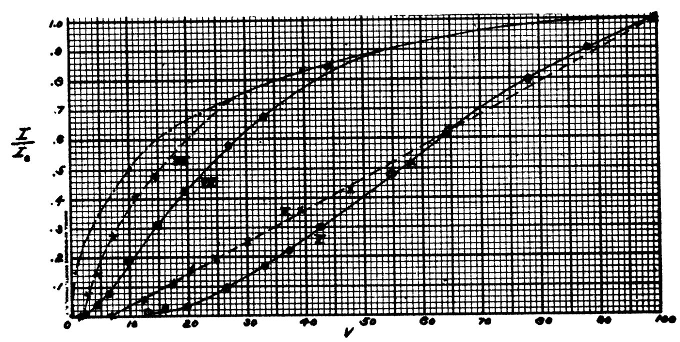

Fig. 11.

April 6, 1920. $d = 1.66$, $K = 2.16$, $n = 4 \times 10^5$.
V. $p = 76.5$ $N = 726$
VII. $p = 33.0$ $N = 742$
Observed x...x...
Computed -o———o-
Saturation —. —. —. —.

given, as dotted curves with crosses, the corresponding values of I/I_0 plotted against the voltage V as actually determined experimentally.[1] The curves represented by the dash dot lines, with no points marked, are in each case the actual saturation photo-electric current curves taken at the time of the experiment.

[1] The values of I/I_0 for the experimental curves were determined from the experimental curves by reducing the electrometer deflections actually measured to fractions of the apparent "saturation" value of the current. For measurements where the curves struck the axis below 40 volts this saturation value of the current was generally taken as the deflection at 100 volts accelerating potential. In some cases however it was taken from the half value of the "control" deflection at 100 volts. The two are closely the same for at 100 volts under most conditions of measurement the number of the carriers reaching the plate E in a given time of exposure to the alternating potential is practically equal to the number that reach E at the same voltage when the direct accelerating potential is on for half the time. The reason for reducing the readings with the direct potential to half is that with the alternating accelerating potential the field is on for but half the time of exposure. A typical transformation of the curves actually obtained may be seen in the case of the curves of Fig. 3 which are the curves of Fig. 2 as experimentally obtained reduced in the manner above indicated. In any case the changes produced near the feet of the curves by such a transformation are small and it is these parts of the curves which are of greatest importance.

The curves shown in Fig. 4 are the observed and the computed curves obtained at a pressure of 95 mm. with different frequencies. Figs. 5, 6 and 7, give the observed and computed curves taken on another sample of air with varying pressures and frequencies. The value of n used in the computation of both these sets of curves was 2.5×10^5. In the Figs. 8 and 9, as well as in the Figs. 10, 11 and 12, are given the observed

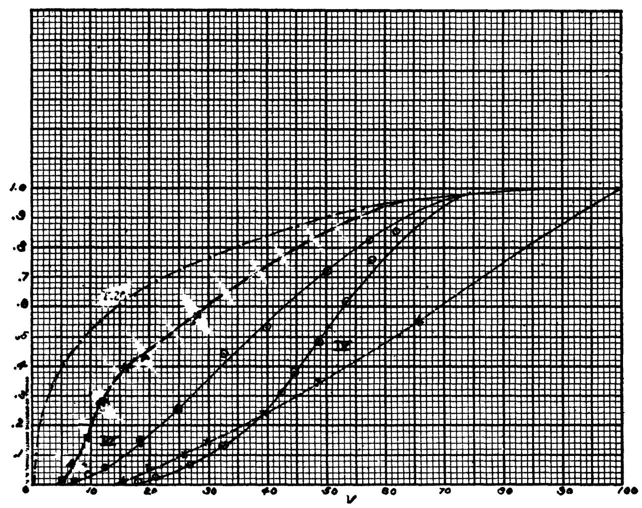

Fig. 12.

April 6, 1920. $d = 1.66$, $K = 2.16$, $n = 4 \times 10^5$.
IV. $p = 97$ $N = 376$
VI. $p = 55$ $N = 742$
Observed x. . . x. . .
Computed -o———o-
Saturation —. —. —.

and computed curves for two sets of determinations in air at varying frequencies and pressures, whose computed curves were obtained assuming a value of $n = 4 \times 10^5$. In all cases the legend gives the conditions under which the determinations were made, and the points illustrated are the actual points obtained. A number of other sets of determinations have been computed and compared with the experimental results with the same degree of success.

In examining the curves two points stand out prominently. First barring the upper portions of the curves taken at or near atmospheric pressure (where for reasons to be given later the curves should not agree) there is fair agreement between the general forms of the observed and computed curves: That is to say there is sufficient similarity in the form of the curves and in their variations with r and N to justify the assumption that they correspond to an equation of the type used. Secondly it can be observed that the values of the voltage at which the ratio I/I_0 reaches some definite low value (*e.g.*, $I/I_0 = .02$ near the limit of measurement of the electrometer), are quite closely the same for the observed and the corresponding computed curves. *Since it is these portions of the experimental curves* (which one may term the feet of the curves), *which yield the values of V_0 corresponding to abnormal mobilities, it is obvious that the curves deduced on the basis of the results of the theory of J. J. Thomson yield values of V_0 quite well in accord with those actually observed.* The theory of Thomson then is in a certain measure well able to predict the anomalous mobilities found for the negative ions for low pressures, which have been the cause of so much discussion.

The reason for the failure of the curves to fit at their upper portions is as follows: At first sight one would expect the curves which are obtained at atmospheric pressure (where the carriers are for the most part normal ions from the beginning), to follow the saturation current curve with decreasing voltage until a value of V is reached, at which in the time of an alternation the carriers can just cross from the plate P to E. At this voltage, V_0, the current should abruptly fall to 0. This condition is implied in the application of the Thomson theory for in the development of that theory it is assumed for simplicity that as soon as V is such that $V = d^2/uT$ *the ions of mobility u all get across.* This is not the case in practice. Starting at a value of the alternating potential equal to V_0 in the negative phase on P, only those carriers will get across to E that were liberated in the first instants of that phase. For carriers liberated in the later portions of that phase will not have time enough to reach E under the existing field. On the reversal of the field such later ions will be all dragged back to the plate P and lost. As V is increased carriers that are liberated later, and later in the negative phase of the potential will succeed in crossing. So that the current to E will approach a sort of saturation value when V_0 has been considerably exceeded. The experimental curve would then not be expected to rise nearly vertically at V_0 as assumed, but would be expected to *begin* to rise at this value and then to gradually increase reaching a maximum at values of V a good deal higher than V_0. Such, as is well known, is actually the case.

In the case of the Franck modification of this method the curves are more like the theory, for only a part of the ions which are driven back to the plane of the gauze are absorbed by it while a plate, as distinguished from a gauze, will absorb them all.

Because of the presence of carriers which are electronic for a considerable portion of their path between the plates as the pressures are reduced below 200 mm. the curves obtained on the basis of the Thomson theory with its simplifying assumption become themselves increasingly inclined to the vertical below this pressure. This has for a result that the differences in shape of the computed and the observed curves becomes much less marked at the lower pressures, as is readily seen.

There is however another point in which the curves do not conform. This is noticeable in Figs. 5, 6, and 7, where the constant n was taken as 2.5×10^5. While the feet of the curves at pressures above 59 mm. coincide quite well for the theoretical and the observed results, it is seen that the feet of the experimental curves below 59 mm. lie at voltages well *below* those for the computed curves. In other words the "anomalous" portions of the experimental curves actually seem to develop more rapidly with decreasing pressures than the theory would predict. This tendency is seen in the curves represented in Figs. 8 to 12, where the value of n chosen was 4×10^5. In this case the feet of the curves at 59 mm. coincide reasonably well, while the feet of the experimental curves taken for 80 and 100 mm. lie at *higher* voltages than the corresponding theoretical curves. In other words the *higher* value of n causes a closer agreement between the curves at the *lower* pressures, than at the higher ones. Accordingly n does not seem to be constant but appears to increase with decreasing pressure. This was the result obtained throughout in computing n. The curves at the lower pressures from 20 mm. to 60 mm. yielded values of n from 9 to 4×10^5, while the curves for pressures between 60 mm. and 130 mm. yielded values of n ranging from 4.0 to 1.5×10^5. The value of n was computed from the theory, and is subject to the condition that the assumptions of the theory are fulfilled. Now J. J. Thomson assumed that the velocity of the electron produced by the field between the plates was *negligible* compared to the velocity w which it possessed in virtue of its kinetic energy of agitation. Now w at 20° C. is about 1.2×10^7 cm./sec., while the velocity acquired between impacts in a field of 10 volts per cm., at 30 mm. pressure lies in the neighborhood of 7.1×10^6 cm./sec., *i.e.*, it is about half of w. If in addition it be considered possible that the velocity thus acquired in the field is not completely wiped out at each impact (*e.g.*, due to quasi-elastic impacts between electrons and nitrogen molecules) one sees how at considerably higher pressures the conditions assumed by the theory may not be met. Such elastic impacts were observed between electrons and hydrogen molecules by Franck (8) and Hertz, and Compton (9) states that they may also be possible in the case of impacts with oxygen molecules though to a much less degree than in hydrogen. In fact Wellisch (1) uses this concept as a possible explanation of some peculiar results obtained in studying the mobilities of electrons. The writer in assuming the value of K' to be a constant of about 200 cm./sec. in value introduced any variation in K', due to the causes above considered, into n. One must then ascribe the deviations of these results from the theoretical ones not to variations in n but to the causes above outlined. In choosing a value for n for future reference it is best, in view of this increase of n with lower pressures, to choose the value of n which was determined at the lower range of pressures (*i.e.*, $n = 2.5 \times 10^5$), where less errors are introduced into the assumptions.

From the above curves one is justified in concluding that *these results furnish a strong qualitative verification* of the J. J. Thomson theory of ion formation.

Correlation of Thomson Theory with Results of Wellisch.

Having now obtained evidence for the correctness of the Thomson theory it remains to correlate these results and the theory with the apparently contradictory results of Wellisch. The essential difference between the present experiments and those of Wellisch lies in the fact that Wellisch using the *Franck modification* of the Rutherford alternating

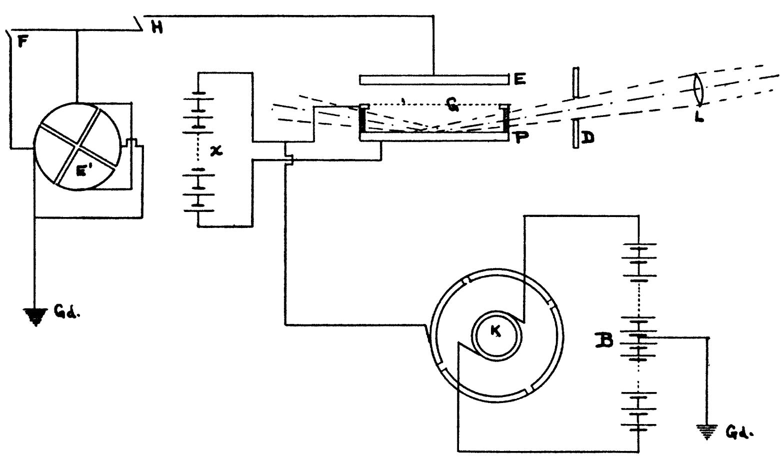

Fig. 13.

current method generated his ions by means of alpha particles in a sort of auxiliary chamber PG, Fig. 13. Furthermore Wellisch in general worked at pressures well below those of the other workers.

In an auxiliary chamber such as PG electrons liberated in the process of ionization have to travel distances as great as 2 cm. in air in fields of about 8 volts per cm. They thus make many collisions with neutral molecules before passing through the meshes of the gauze G into the measuring field GE. Accordingly on the Thomson theory there must be quite a proportion of carriers which though starting as electrons form attachments by virtue of their many encounters and therefore enter the space GE as ions. These, in measurements of the Wellisch type, give mobilities which are perfectly normal, *i.e.*, the measured mobility should be inversely proportional to the pressure. Besides such carriers there

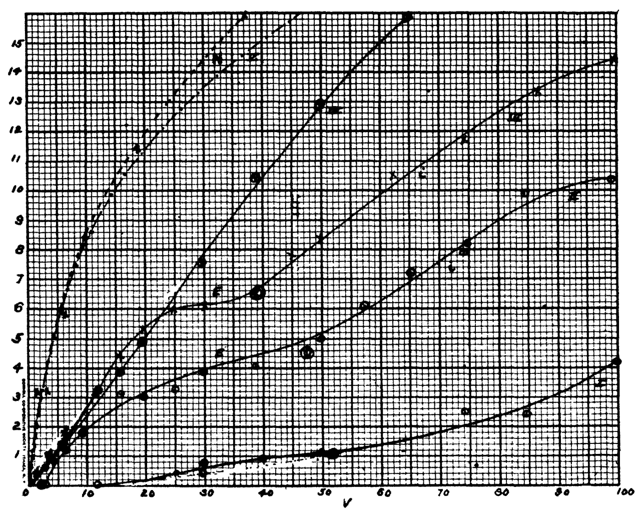

Fig. 14.

May 21, 1920. Using auxiliary gauze G 1.5 cm. above P, d = 1.33, p = 49 mm., N = 710.

I. X = 1.5 volts Mobility K = 1.65
II. X = 4.5 " " K = 1.80
III. X = 9.0 " " K = 2.20
IV. X = 45.0 " " ....
V. X = 45.0 " Saturation —. —. —. —.

Anomalous mobility K' for all about 33.0. N curve ...... for free electrons in N_2 gas at atmospheric pressure. N = 360.

enter the field GE through the gauze electrons, which increase in relative numbers as the pressures decrease. These should behave just as did the photo-electrons in the experiments of the writer in giving anomalous mobilities as the Thomson theory demands. The result to be expected on applying the Thomson theory to the method employed by Wellisch would then be that the current-voltage curves obtained consist of the two parts i and E of curves II. and III., Figs. 14, 15, 16, and 17. The part due to the ions (i) should yield at its lower extremity (*i.e.*, at the point of inflection) mobilities inversely proportional to the pressure; while the other portion (E) due to electrons uniting to form ions in going from G to E should yield the anomalous mobilities previously observed.

Now Wellisch in his experiments found curves consisting of two distinct parts which were quite similar to the curves represented above. He showed that the upper portions of his curves, corresponding to the portion of the curves marked i in Fig. 14, yielded values for the mobility-constants of the carriers which they represented equal to those of normal ions. These mobilities moreover were inversely proportional to the pressure. Wellisch however did not find that the feet of the E portions of the curves were due to carriers yielding the fictitious abnormal mobili-

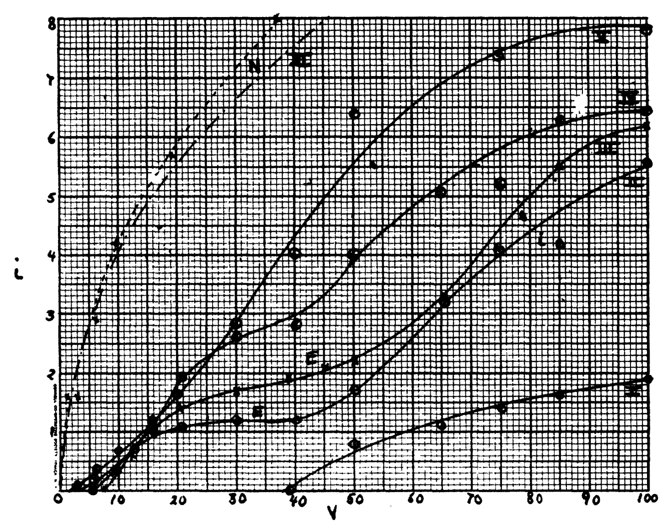

Fig. 15.

May 22, 1920. Using auxiliary gauze G 1.5 cm. above P, d = 1.33, p = 56 mm.

I.	X = 4.5 volts	N = 710	Mobility	K = 2.05
II.	X = 9.0 "	N = 710	"	K = 1.90
III.	X = 13.5 "	N = 710	"	K = 1.70
IV.	X = 22.5 "	N = 704	"	K = 2.05
V.	X = 45.0 "	N = 704	"	K = 2.20
VI.	X = 45.0 "	N = 0	Saturation	–. –. –. –.

Anomalous mobility K' for all curves is about 19. N curve ...... for free electrons in pure N_2 gas at atmospheric pressure and N = 360.

ties as required by the Thomson theory. In fact in most of his published curves the feet of his E curves cut the axis so close to the O value that he ascribed them to electronic carriers which remained *permanently free.* It was this interpretation of his curves that lead Wellisch to the theory of ion formation proposed by him.

It is then clear that to correlate the Wellisch experiments with the Thomson theory one must show that the E portions of Wellisch curves are not due to *permanently free electrons* as Wellisch was led to believe but are due rather to the attachment, *while in the measuring field of electrons to molecules to form ions*. In consequence of the low pressures employed by Wellisch it is impossible to estimate from the intercepts of his curves with the voltage axis whether the values of the mobility-constant K' for the E type of carrier were of an electronic order of magnitude (*e.g.*, above 200 cm./sec.) (1, 7) or whether they had values of the order of magnitude which the Thomson carriers yield at those pressures.

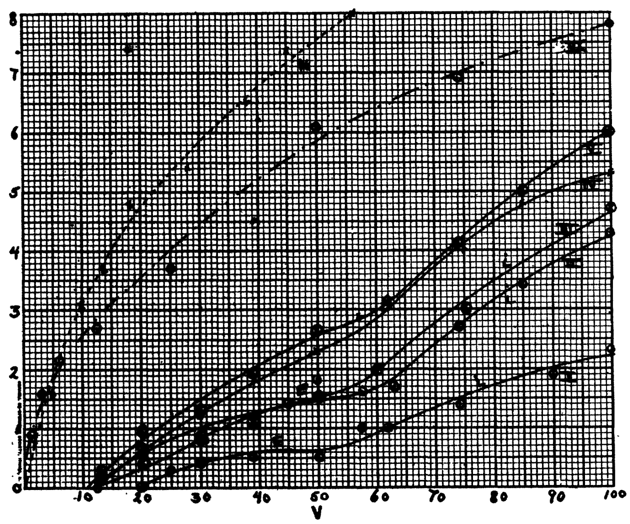

Fig. 16.

Oct. 15, 1920. Using auxiliary gauze G 1.5 cm. above P, d = 1.28, p = 75 mm.

I.	X = 4.5 volts	N = 658	Mobility K = 1.98
II.	X = 9.0 "	N = 658	" K = 1.98
III.	X = 18.0 "	N = 658	" K = 1.98
IV.	X = 45.0 "	N = 658	" K = 1.98
V.	X = 85.5 "	N = 658	" K = 1.98
VI.	X = 13.5 "	N = 0	Saturation —. —. —. —.

Anomalous mobility K' for all curves about 9.3. Curve labeled N free electron curve for N_2 gas at atmospheric pressure with N = 147. Curve ......

The experiments of Wellisch were accordingly repeated by the writer using pressures ranging from 34 mm. to 84 mm. (*i.e.*, where the anomalous mobilities lie between 100 and 5 cm./sec.) with a view determining from the intercepts of the E portions of the curves with the voltage axis whether the carriers yielded mobility constants K' of electronic or ionic magnitudes.

The apparatus of the writer was accordingly converted into one of the Wellisch type using photo-electrons as a source of ions. This was accomplished by interposing the gauze G, Fig. 13, between the plate P and the plate E. The distance PG was 1.5 cm. and the distance GE was 1.30 cm. A steady potential difference X was maintained between P and G by means of a battery of small flashlight cells, x, in such a sense as to drive negative carriers liberated at P through the meshes of the gauze G. If for a fixed value of the field X a series of measurements was made of the current to the electrometer plate E, for various values of the alternating potential applied to the gauze, curves were obtained of the type found by Wellisch. A series of such curves using different values of the field X varying from 1.5 to 85.5 volts was obtained for a number of pressures ranging from 34 mm. to 84 mm. Four typical sets

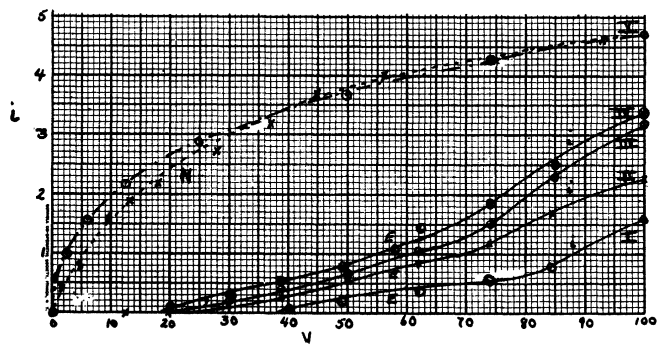

Fig. 17.

Oct. 16, 1920. Using auxiliary gauze G 1.5 cm. above P, d = 1.28, p = 84 mm.

I.	X = 4.5 volts	N = 660	Mobility K = 1.89
II.	X = 13.5 "	N = 660	" K = 1.89
III.	X = 27.0 "	N = 655	" K = 1.89
IV.	X = 85.5 "	N = 650	" K = 1.89
V.	X = 45.0 "	N = 0	Saturation –. –. –. –.

N. Curve for free electrons in N_2 gas at atmospheric pressure with N = 146. Curve dotted .... Anomalous mobility K' for all curves about 6.4.

of curves are represented in Figs. 14, 15, 16, and 17 in which electrometer deflections in cm. are plotted against the alternating potential. These figures include as well the saturation photoelectric curves at those pressures, and the characteristic curve (N) yielded by purely electronic carriers (permanently free electrons), obtained in nitrogen at atmospheric pressure. The values of X as well as other data concerning the curves are given in the legend.

It is obvious at once that as the pressure increases in Figs. 14, 15, 16, and 17 the asymptotic feet of the E portions of all curves have their points of inflection (or intercepts with the V axis where points of inflection are poorly defined) at higher and higher values of the voltage, which is a characteristic of the Thomson type of carrier. It is also patent that in no case do these portions of the curves follow the free electron curve obtained in nitrogen. If the average value of the fictitious abnormal mobility of these curves be estimated from the points of inflection, or intercepts, they yield the values 33, 19, 9.3, and 6.4 cm./sec. which are similar to those obtained for carriers in the absence of the gauze at these pressures and frequencies.

The variation in form of the Wellisch type of curves with the field X, which is obvious when one regards the set of curves for any one pressure, may be simply explained on the Thomson theory. If the values of X are low the ions spend considerable time in the auxiliary field PG before reaching the gauze G. In this time they make many impacts with neutral molecules. On the Thomson theory it is to be expected that the greater proportion of carriers passing through the gauze under these conditions would be normal ions. This is seen to be the case in curves numbered I, Figs. 14 and 15. As X increases and the time spent in PG is therefore decreased more and more electrons succeed in reaching G without attachment. The E portions of the curves consequently increase in relative importance as in curves II. and III., Figs. 14, 15, 16. On still further increasing X it is possible to cause most of the electrons to reach G without attachments. One has then precisely the conditions obtained in the absence of the gauze, curves having but one part E being observed. These are found in curves IV., Fig. 14, and V., Fig. 15. If the pressure be reduced the effect on the form of the curve is the same as is produced by increasing X, for the time spent in PG is therefore reduced.

From the foregoing one must conclude that not only is there no contradiction between the results of Wellisch, and those of the other workers, but the results of Wellisch are actually in accord with the theory of Thomson. The apparent discrepancy lay therefore only in the *interpretation* of the E portions of the Wellisch curves. Having then shown that the process of ion formation in air probably consists as Thomson postulated in the attachment of an electron to a neutral molecule which happens in one out of about 2.5×10^5 collisions, one may be permitted to speculate on the conditions determining this attachment. It has been shown by Franck (7), and also recently by the writer (10), that the electrons do not attach to form ions in pure nitrogen gas. And since the curves obtained in pure oxygen, as well as those in nitrogen contaminated with small quantities of oxygen, yield values of n of the same order of magnitude as those in air (when they are calculated back to air on the basis of their oxygen content), one may safely conclude that it is to the oxygen molecule in pure dry air that the electron attaches itself to form the negative ion. One must then picture the process of ion formation as resulting from the particular conditions surrounding the impact of an electron with an oxygen molecule, these conditions being fulfilled on the average in only one out of approximately 50,000 impacts. The nature of these conditions furnishes a problem for the future. These conditions may consist in the electrons striking a certain electronic ring in the molecule under just the right conditions of velocity. They may consist in the molecule struck being in a certain chemical or physical state, *e.g.*, ozone, or in some particular state as regards radiation, as is suggested by Perrin (11) for chemical phenomena. It is hoped that some data may shortly be available on the effect of the energy of the electron on this process. Some light will also be thrown on this process from the investigation of the behavior of other gases in this respect. Work is now under way in an attempt to determine n for different gases, and to correlate this with their chemical nature.

The writer in concluding desires to express to the National Research Fellowship Board his sincere thanks for the opportunity given him, as National Research Fellow, to clear up a problem which has fascinated him for a number of years. He also wishes to express his gratitude to Professor R. A. Millikan for the excellent facilities he placed at the writer's command for pursuing this work in the Ryerson Laboratory as well as for his kind advice and criticism in the writing of this paper.

Note Added Dec. 30, 1920.

Recent results obtained in this laboratory by Mr. Wahlin show definitely that the energy imparted to the electron is not a factor in determining its attachment to a neutral molecule to form the negative ion in air. Although Mr. Wahlin subjected electrons to fields varying from very low values up to values such that they acquired energies causing ionization by collision no noticeable increase in the formation of ions could be observed. These results definitely indicate that the theory of ion formation proposed by Wellisch is untenable.

Summary.

1. Experimental work was undertaken to attempt to decide between the two theories of negative ion formation, from electrons and neutral molecules, proposed by J. J. Thomson and by Wellisch.

2. Mobilities of the carriers formed by photo-electrons liberated from one plate of a parallel plate condenser by a beam of ultraviolet light, focussed on it at a glancing angle by a quartz lens, were determined at different pressures for air using the Rutherford alternating current method.

3. The results in general confirmed the results of previous observers, yielding a single class of carriers whose mobilities became abnormal below pressures of 150 mm. The value of these mobilities was also found to be a function of the frequency of commutation in agreement with earlier results.

4. The manner of introduction of the ultra-violet light into the chamber having reduced the " stray light " effects, it was found that the asymptotic feet of the curves observed below 200 mm. pressure were a real and important feature of the phenomenon.

5. The mathematical theory of J. J. Thomson was adapted to fit these measurements; and on the basis of the equation so deduced the chance of ion formation, n, was determined from experiment.

6. Within the limits of accuracy of the method n was found to be equal to about 2.5×10^5 for pure dry air.

7. The current-voltage curves computed on the basis of the Thomson theory were compared with the observed curves and marked general similarities were noticed below 200 mm. pressures.

8. The asymptotic feet of the computed and observed curves lie close together; which is significant inasmuch as it is these portions of the observed curves that yield the abnormal values of the mobility.

9. Deviations of the observed curves from those computed at the higher and the lower pressures are explained.

10. Repetition of the Wellisch experiments shows that what he termed "free electrons" are the carriers of abnormally high mobilities observed by the earlier workers.

11. It was also shown that the identity of Wellisch "free electrons" with the carriers changing from electrons to ions in the measuring field once established, the other results of Wellisch are to be expected on the Thomson theory.

12. It is shown that as the electrons do not attach to N_2 molecules, and that as the values of n obtained in pure O_2 and in N_2 with small quantities of O_2 in it agree with the values found for air on the basis of its oxygen content, one must conclude that it is to the O_2 molecules in air that the electrons attach. The value of n for O_2 molecules is then 50,000.

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