the particles from the radium C had to travel through a little over a centimetre of air before reaching the reflector. The reflected particles had still an appreciable velocity, since, by interposing an aluminium foil of thickness equivalent in stopping power to $\frac{1}{2}$ cm. of air, the number of scintillations counted was not changed. This might be expected from Experiment (II), which showed that the α-particles are reflected from a relatively thin surface layer of the reflector.

We are indebted to Prof. Rutherford for his kind interest and advice throughout this research.

The Passage of Electricity through Gaseous Mixtures.

By E. M. WELLISCH, M.A. (Sydney), Emmanuel College, Cambridge.

Introductory.

According to the current theory with regard to the production of ions in a gas subjected to the action of Röntgen rays, the act of ionisation consists in the expulsion of one or more corpuscles (*i.e.* negatively charged units of electricity) from each of a certain number of molecules constituting the gas. The residual portion of each of these molecules is then said to be positively charged, although the nature of this charge is not in any way specified. There are thus present in the gas negatively charged nuclei (*i.e.* the expelled corpuscles) and positively charged nuclei (the residual portions of the ionised molecules); owing to the forces due to electrostatic induction these nuclei attract several of the gas molecules, and the resulting molecular aggregates constitute the gaseous ions, both negative and positive.

Suppose, now, that a mixture of two gases, *e.g.*, sulphur dioxide and oxygen, is subjected to the action of Röntgen rays; the positive nucleus would be of greater volume and mass in the case of sulphur dioxide than of oxygen, and in consequence it is quite possible that the resulting ions should show similar differences. Accordingly, if the two groups of positive ions move in the same electric field, a difference in velocities might thus reasonably be expected.

The object originally proposed in the present series of experiments was to

ascertain whether the ions of each sign produced by Röntgen rays in a mixture of two gases, or of a vapour and a gas at normal temperatures, possessed two distinct mobilities when influenced by an electric field.
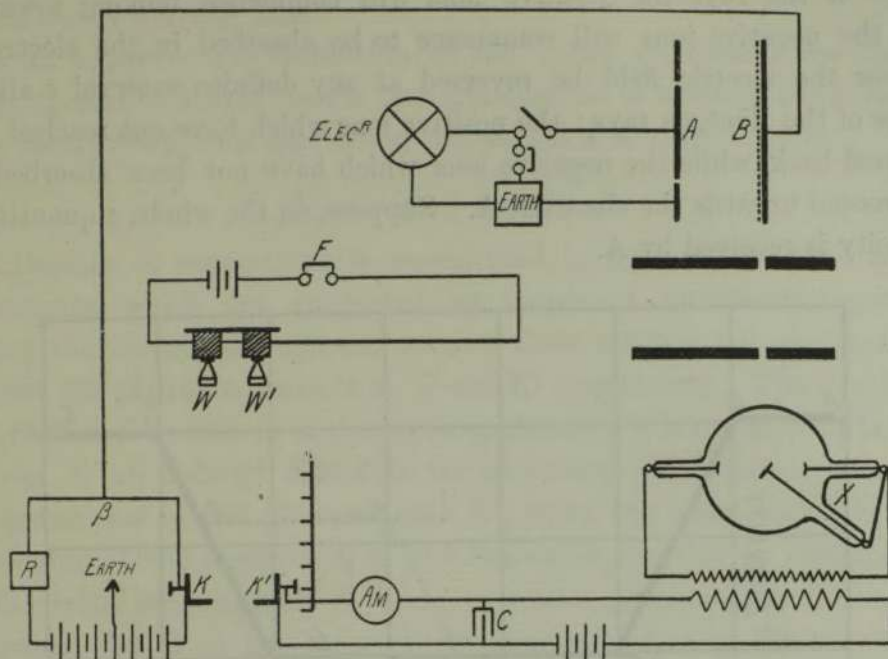

FIG. 1.

Experimental Method.

It was found that Langevin's method as ordinarily applied, and of which a description is given in a recent paper by the writer,* was not exactly suited for the purposes of the present investigation. On this account a modified form of Langevin's method was devised. The ionisation chamber consisted of a cylindrical brass vessel with an aluminium bottom; inside the chamber were two rectangular aluminium electrodes B and A (fig. 1), which were connected respectively to a source of potential and to an electrometer by means of wires led out through ebonite plugs, the electrode A being surrounded by an aluminium guard ring. The dimensions of B were 23 by 6 cm., and of A were 7 by 4 cm.; the two electrodes were placed in a vertical position, and at a distance from one another of 31 mm. The inside of the chamber was lined with paper so as to minimise effects due to secondary radiation. A single flash of Röntgen rays of very short duration was sent through a slit between two rectangular plates of thick lead; after passing through another similar slit the rays then passed into the ionisation chamber, grazing the electrode B. A narrow layer of ions was thus formed in the gas or gaseous mixture in the vicinity of the electrode B. The lead

plates were adjustable, so that both the position and the width of the slit could be readily altered. Suppose, now, that the electric field is such that the force on a positive charge is from B to A; then immediately after the passage of the rays the positive ions will commence moving towards A, while the negative ions will commence to be absorbed in the electrode B. Let now the electric field be reversed at any definite interval t after the passage of the Röntgen rays; the positive ions which have not reached A will be turned back, while the negative ions which have not been absorbed in B will proceed towards the electrode A.   Suppose, on the whole, a quantity Q of electricity is received by A.
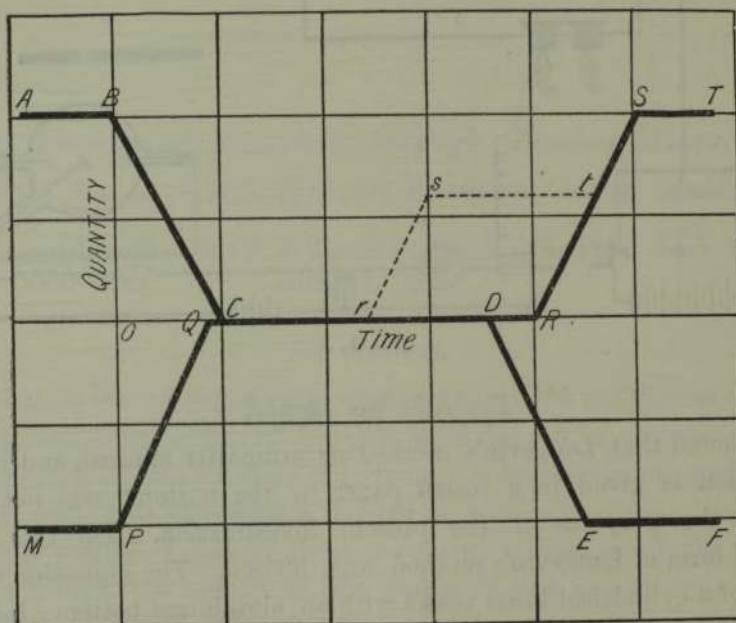

Fig. 2.

The curves connecting Q and t will be of the character given in fig. 2; the curve MPQRST refers to the case when B is positive before reversal, and the curve ABCDEF to B negative before reversal; the oblique portions of the curves correspond to the finite width of the layer of ions, while the part that lies along the time axis occurs when the field is reversed after all the negative ions have been received at B, and before any of the positive ions have reached A. The distance between the points on the time axis corresponding to the points P and S represents the time taken for a positive ion to traverse the known distance from B to A; hence the actual velocity can be calculated. If there were two distinct mobilities, *e.g.*, as might be expected for the ions in a mixture of two gases, then the ions would begin to separate

as soon as the rays had passed, and the actual curve obtained would be of the form MPQ*rst*ST, in which the point *s* corresponds to the receipt by A of all the positive ions of larger mobility, and the point S to the receipt of all the more slowly moving ions.

Thus an experimental realisation of the curve expressing the relation between Q and *t* should decide the question as to whether there are two distinct mobilities for the ions of any one sign in a mixture of gases.

Experimental Procedure.

The diagram of connections is represented in fig. 1; W and W' are two iron weights, which are supported by means of an electromagnet; on breaking the circuit through the magnet these weights fall simultaneously and break the platinum contacts at K and K' respectively. The breaking of the contact at K', which is in the primary circuit of a Marconi induction coil, gives rise to an induced E.M.F. in the secondary, and causes a momentary discharge to pass in the Röntgen bulb X; when the contact at K is broken the potential of the electrode B of the ionisation chamber is reversed, as is manifest from the diagram, R being a water resistance of the order of a megohm, and B at the moment of breaking being at the potential of the point β. The time interval between the Röntgen ray flash and the subsequent reversal of potential could be adjusted by suitably fixing the position of K' with regard to a graduated vertical scale; the actual values of the time interval were calculated by means of the ordinary formula for a body falling freely under gravity. The bottom of the falling weight W was at a height of 54·8 cm. above the contact K. C is a capacity of about 7 microfarads inserted in parallel with the primary of the induction coil in order to prevent sparking at the contact K'; when the spark was entirely eliminated, and when the current through the primary of the induction coil was kept constant, the intensity of the Röntgen ray flash was sensibly constant at each discharge. A Dolezalek electrometer with a fine platinum suspension was employed in order to measure the ionisation produced; with the needle charged to a potential of 80 volts, the electrometer afforded a deflection per volt of 620 mm. on a scale about 1 metre distant.

In the previous paper (*loc. cit.*) a brief discussion is given with regard to the theoretical assumptions and experimental difficulties in connection with Langevin's method; for a more detailed account the reader is referred to Langevin's original memoir.[*]

A single reading was taken in the following manner:—

(i) K' is adjusted to the required height on the scale.

[*] 'Ann. de Chim. et de Phys.,' VII, vol. 28, p. 495, 1903.

(ii) The electrode A and the quadrants are earthed and the contact K is
    made.

(iii) The magnet circuit is completed at F; the weights W and W' are
    placed in position; the electrode A is insulated, the quadrants
    remaining earthed.

(iv) The contact K' is made; the magnet circuit is broken, allowing the
    weights to fall and break the contacts K and K'.

(v) After the weights have fallen, the ions will have had sufficient time
    to be all received at the electrode; the contact at K is then remade.

(vi) The total quantity received by A is then measured on the electro-
    meter.

The gases employed were all carefully dried before passing into the
ionisation chamber. The chamber was exhausted by means of a water pump
and a Töpler mercury pump, and the gas or vapour passed into it in the
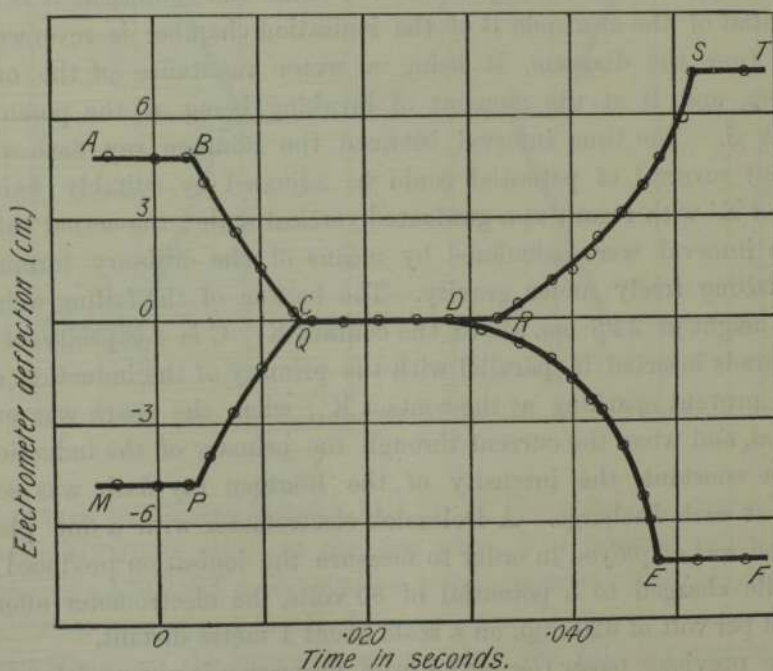manner described in the previous paper.

Time in seconds.

Fig. 3.

Experimental Results.

Sulphur Dioxide and Oxygen.—The first mixture of gases investigated was
that of sulphur dioxide (pressure 131 mm.) and oxygen (629 mm.); the
pressures being chosen so that each constituent gas afforded practically the
same ionisation from the flash of Röntgen rays. The curves obtained are

given in fig. 3 ; these correspond to positions of the slit between the lead plates, so that the layer of ions produced by the Röntgen ray flash did not graze the electrode B ; the width of the slit between the plates was about 3 mm. It is noticeable that there is no evidence of the existence of a portion of the curve corresponding to the part *rst* in fig. 2. The curvature of the oblique portions is due probably to non-uniformity in the distribution of the ions. In the present instance, the fall of potential across the electrodes was 242 volts, and the times taken for the positive and negative ions to traverse a distance equal to that (31 mm.) between the two electrodes were 0·0551 and 0·0519 sec. respectively, these time intervals corresponding to the sum of the abscissæ of the points B and S in the case of the positive ion and P and E in the case of the negative ion. The resulting mobilities are 0·72 cm./sec. for the positive ion and 0·76 cm./sec. for the negative ion.

The curves in fig. 3 are typical of other curves which were obtained for the same mixture corresponding to different positions and different widths of the slit.

Ethyl Ether and Air.—Fig. 4 represents similar curves obtained for a mixture of ethyl ether (122 mm.) and air (508 mm.), the pressures being
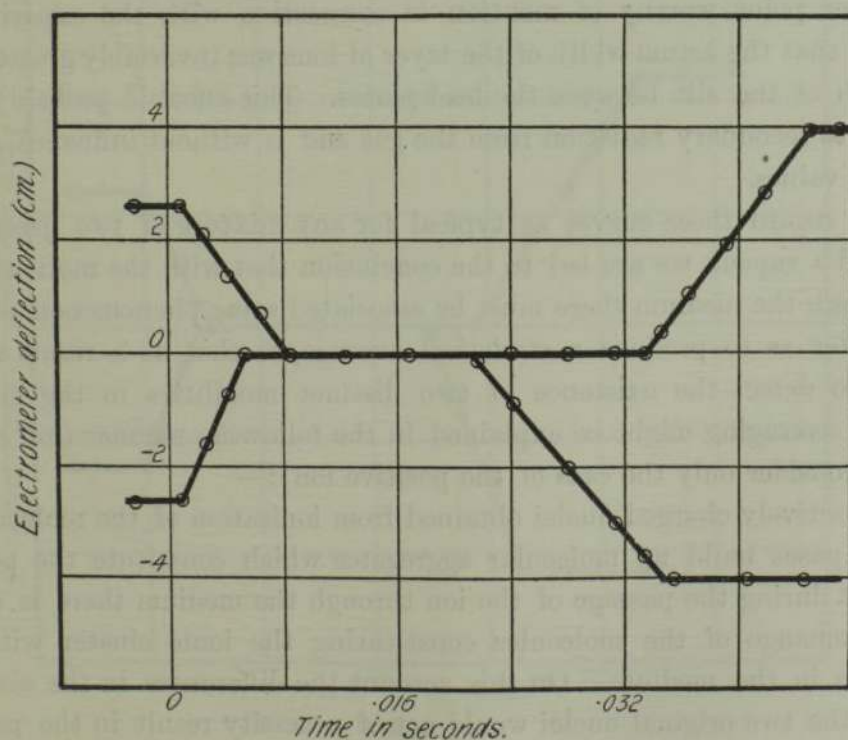

FIG. 4.

again so chosen that the ether and the air afforded practically the same ionisation from the flash of Röntgen rays. In this case, again, there was no evidence of two distinct mobilities either for the positive or for the

negative ions.   The fall of potential across the electrodes was 202 volts, and the calculated times required for the positive and negative ions to traverse the distance between the electrodes were 0·0457 and 0·0353 sec. respectively. The mobilities of the positive and negative ions at the actual pressure of 630 mm. were 1·04 and 1·35 cm./sec. respectively.   Several other series of curves were drawn with different widths and different positions of the slit, but in no instance was there evidence of two distinct mobilities either for the positive or negative ions.

In connection with the experimental curves, it is worthy of notice that the ordinates of the points P and B are each less than the ordinates of the points S or E, whereas in the theoretical curve the ordinates are represented as being of equal length.   This is due to the distortion of the electric field which occurs on the reversal of potential, the electrode A being now no longer at zero potential, and some of the lines of force in consequence passing over to the guard ring, which is earth connected.   The electrode A will therefore receive only a fraction of the total number of ions which are formed near B, the remainder being received by the guard ring.   The mobility values are, however, unaltered, as the abscissæ of the points P and B are not affected.

Another point worthy of mention in connection with the experimental curves is that the actual width of the layer of ions was invariably greater than the width of the slit between the lead plates.   This effect is probably to be ascribed to secondary radiation from the gas and is without influence on the mobility values.

If we regard these curves as typical for any mixture of two gases or of a gas and a vapour, we are led to the conclusion that with the motion of the ion through the medium there must be associated some phenomenon of such a character as to produce a statistical average, so that as a result we are unable to detect the existence of two distinct mobilities in the mixture. Such an averaging might be explained in the following manner (for brevity we will consider only the case of the positive ion):—

The positively charged nuclei obtained from ionisation of the molecules of the two gases build up molecular aggregates which constitute the positive ions; but during the passage of the ion through the medium there is a continual exchange of the molecules constituting the ionic cluster with the molecules in the medium.   On this account the differences in the size and mass of the two original nuclei would not of necessity result in the positive ions having two distinct mobilities.   This is the conclusion at which M. Blanc* arrived as a result of his experiments on mobilities in gaseous mixtures, in particular the experiment in which an ion formed in carbon

* 'Journ. de Phys.,' vol. 7, p. 838, 1908.

dioxide and passed through air was shown to have the same mobility as an ion formed in air and passed through air.

The experimental results to be described later lead, however, to an entirely different explanation of the statistical average.

There is an interesting feature in connection with the curves (figs. 3 and 4) which suggests at first sight the existence of an averaging effect. It is noticeable that the distance along the time axis corresponding to the points R and S is greater than the corresponding distance for the points B and C; and similarly that the distance along the time axis for the points D and E is greater than the corresponding distance for the points P and Q; in other words, the ions require a longer time after their arrival at A before they are all received by the electrode A than what is necessary for them to be all received by B after their arrival. It appears, therefore, that the original layer of ions broadens out in its passage through the medium. In order to test this point more completely, curves were drawn with oxygen alone in the ionisation chamber. These curves are given in fig. 5, from which it can be readily seen that the broadening out of the layer of ions occurs markedly for
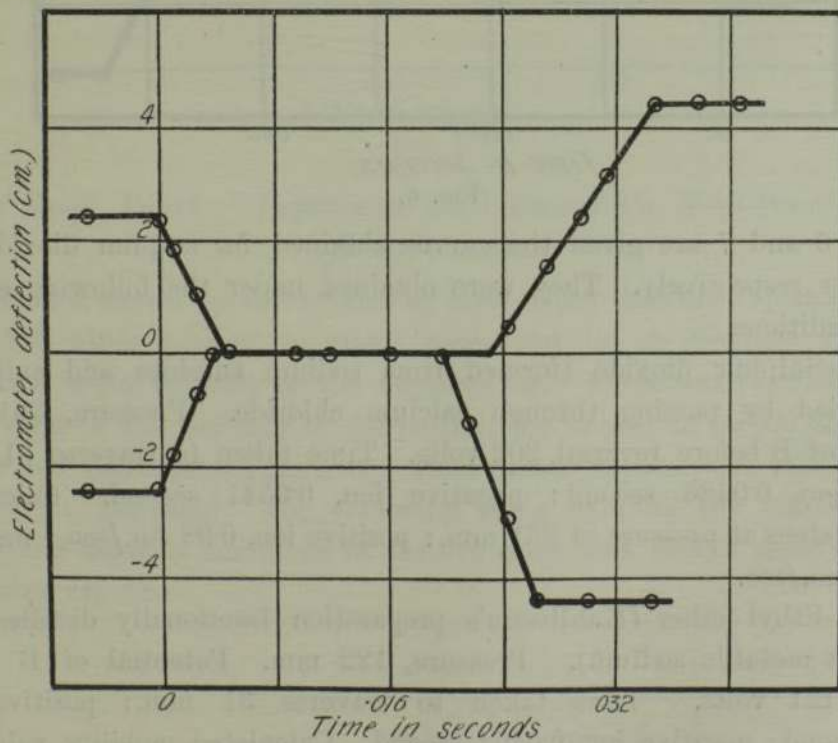

FIG. 5.

the positive ions and to a very small extent for the negative ions; in fact, the small extent in the latter instance is ascribable to the effects of diffusion occurring during the motion of the ions. The writer has hitherto been unable

to assign any definite reason to account for the broadening out of the layer of positive ions, but in this connection it is of interest to note that Franck and Westphal* have recently drawn attention to the existence among the positive ions of a certain percentage which carry a double charge of electricity.
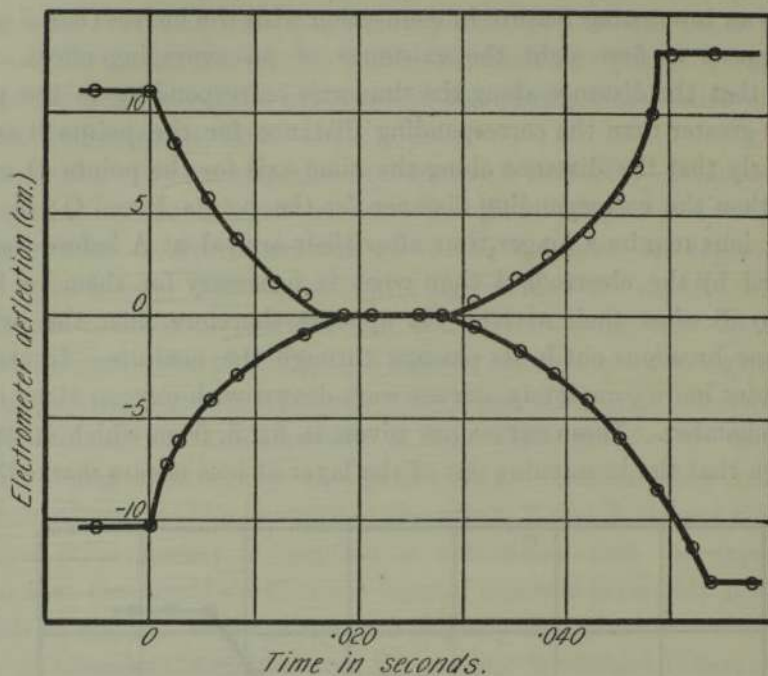

FIG. 6.

In figs. 6 and 7 are given the curves obtained for sulphur dioxide and ethyl ether respectively. They were obtained under the following experimental conditions.

Fig. 6.—Sulphur dioxide (formed from sodium sulphite and sulphuric acid); dried by passing through calcium chloride. Pressure, 331 mm. Potential of B before reversal, 202 volts. Time taken to traverse 31 mm.: positive ion, 0·0486 second; negative ion, 0·0541 second. Calculated mobility values at pressure of 331 mm.: positive ion, 0·98 cm./sec.; negative ion, 0·88 cm./sec.

Fig. 7.—Ethyl ether (Kahlbaum's preparation fractionally distilled and dried with metallic sodium). Pressure, 122 mm. Potential of B before reversal, 121 volts. Time taken to traverse 31 mm.: positive ion 0·0404 second; negative ion, 0·0404 second. Calculated mobility values at pressure of 122 mm.: positive ion, 1·97 cm./sec.; negative ion, 1·97 cm./sec.

It is to be observed that in the case of sulphur dioxide the mobility of the

* 'Verhand. Deuts. Phys. Gesell.,' No. 6, p. 146, 1909.

positive ion is greater than that of the negative, and that in this instance it is the layer of negative ions which appears to broaden out during motion through the gas.
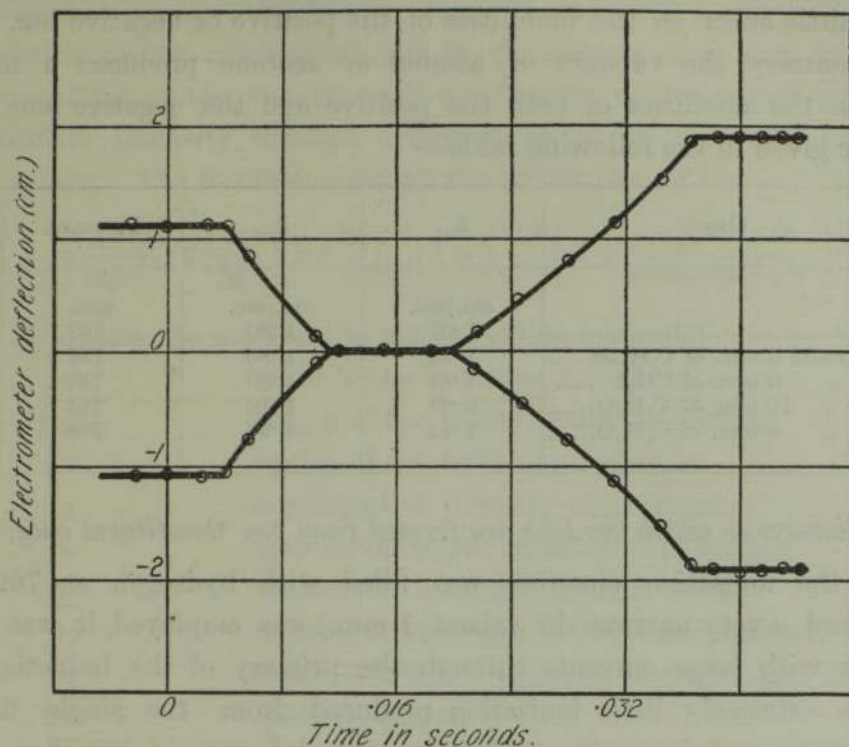

Fig. 7.

Effect of Small Traces of Vapours on the Values of the Mobilities of the Ions formed in Air.

It has been shown by Zeleny and by Rutherford that the vapours of water or alcohol when present in small quantities in air produce a marked diminution in the mobility of the negative ion. There was very little effect on the value of the mobility of the positive ion in air; in carbon dioxide the positive ion increased in mobility when water vapour was added and in hydrogen it decreased. The following table exhibits the values of the positive and negative mobilities in the dry gases and also in gases saturated with water vapour—

Gas.	k_+.	k_-.	Authority.
	cm./sec.	cm./sec.	
Air (dry)	1·36	1·87	Zeleny.
,, (moist)....................	1·37	1·51	,,
Carbon dioxide (dry)	0·76	0·81	,,
,, (moist).........	0·82	0·75	,,
Hydrogen (dry).................	6·70	7·95	,,
,, (moist)	5·30	5·60	,,

A series of experiments was conducted in order to ascertain the effect produced on the ionic mobilities in air by adding small quantities of different vapours; it was found that the vapours of methyl iodide or ethyl bromide had very little effect on the mobilities of the positive or negative ion, while, on the contrary, the vapours of alcohol or acetone produced a marked decrease in the mobilities of both the positive and the negative ions. The results are given in the following table—

Gas.	$k_{+}.$	$k_{-}.$	Pressure.
	cm./sec.	cm./sec.	mm.
Air	1·37	1·80	737
Air and 6 mm. of C_2H_5Br ...	1·32	1·80	737
„ 6 mm. of CH_3I	1·37	1·80	737
„ 10 mm. of C_2H_6O......	0·91	1·10	755
„ 9 mm. of C_3H_6O......	1·15	1·37	755

Mixtures in which the Ions are formed from one Constituent only.

When the ionisation chamber was filled with hydrogen at 760 mm. pressure and a very narrow slit (about 1 mm.) was employed, it was found that even with large currents through the primary of the induction coil there was extremely little ionisation produced from the single flash of Röntgen rays; such ionisation produced a scale deflection of less than 1 mm.

The ionisation chamber was then exhausted to a very low pressure and methyl iodide was passed in till a pressure of 6 mm. was attained; owing to the ease with which this vapour is ionised, on the passing of the flash of Röntgen rays quite a workable deflection (about 30 mm.) was obtained. Hydrogen was then passed in till the total pressure was 760 mm. The mobilities were then measured and the following results were obtained:—

> Negative ion............... 6·86 cm./sec.
> Positive ion .... 5·07 cm./sec.

Another series of experiments in which 12 mm. of methyl iodide was employed gave—

> Negative ion............... 5·96 cm./sec.
> Positive ion .... 4·81 cm./sec.

Zeleny's values for pure dry hydrogen are—

> Negative ion............... 7·95 cm./sec.
> Positive ion .... 6·70 cm./sec.

It appears, therefore, that when the ionisation is all due to the methyl iodide the resulting ions move through a medium which is not sensibly

different from hydrogen with a velocity which approximates to that which would ensue if the ionisation had been due to the hydrogen.

If we consider for the moment the positive ion only and if we regard it as the molecule of methyl iodide with which is associated a charge (e) equal to that carried by the monovalent ion in electrolysis, it is easy to calculate a superior limit to the velocity with which such an ion would move under unit electric intensity through hydrogen at 0° C. and at a pressure of 1 atmosphere. The formula given by the writer (*loc. cit.*) is

$$k = \frac{A\eta}{\rho_1 p} 4\sqrt{2} \left(\frac{m}{M}\right)^{\frac{1}{2}} \left(1 + \frac{M}{m}\right)^{-\frac{1}{2}} \left(1 + \frac{s'}{s}\right)^{-2} \left\{1 + \frac{4(K-1)e^2}{\pi n m v^2 (s+s')^4}\right\}^{-1},$$

here M denotes the mass of the methyl iodide molecule,

m	mass of the hydrogen molecule,
$\frac{1}{2}s'$	radius of the methyl iodide molecule,
$\frac{1}{2}s$	radius of the hydrogen molecule,
η	coefficient of viscosity of hydrogen,
K	specific inductive capacity of hydrogen,
p	pressure of hydrogen in c.g.s. units,
ρ_1	density of hydrogen at 760 mm. pressure,
v	mean velocity of agitation of a hydrogen molecule,
A	quantity $\rho_1 e / m$.

The factor in the curling brackets corresponds to the diminution in mobility resulting from the inductive attraction between the ion and the neighbouring molecules.

The experimental values of the quantities involved in the calculation are $A = 1.30 \times 10^{10}$, $\eta = 85 \times 10^{-6}$, $\rho_1 = 9 \times 10^{-5}$, $p = 1,014,000$,

$$K - 1 = 26 \times 10^{-5}.$$

In order to calculate s'/s it was taken as equal to $\{M/m \cdot d/d'\}^{\frac{1}{3}}$, where d' and d denote the densities in the liquid state of methyl iodide and hydrogen respectively. With $d' = 2.33$, and $d = 0.08$ we have $s'/s = 1.34$. On making the necessary substitutions it is found that the mobility (under 1 volt/cm.) of the methyl iodide molecule through hydrogen is 0·58 cm./sec. if we neglect the diminution in the mean free path due to the attraction of the neighbouring molecules, while if this attraction be taken into account the value of k is 0·15 cm./sec. Of course, any clustering round this molecule as nucleus would produce a further diminution in the value of the mobility. The calculated mobility values, even under circumstances tending to increase the velocity, are thus considerably less than the actual observed mobilities. We are forced to the conclusion that the charge cannot have

been carried throughout by the methyl iodide molecule ; or, in other words, there must have been, at least initially, a transference of the charge from the methyl iodide molecule to a hydrogen molecule.

A similar train of reasoning leads to the necessity of supposing that for the larger portion of its path the negative charge must have been associated with a hydrogen molecule.

Experiments were also performed in which the ions were produced from carbon tetrachloride and mercury methyl and then passed through hydrogen. Results similar to those above described were obtained both for the positive and negative ions.

In the case when 3 mm. of mercury methyl was mixed with 757 mm. of hydrogen and the ionisation was, as before, wholly due to the vapour, it was found that the mobilities of the ions through the mixture were

Negative ion .... 7·18 cm./sec.

Positive ion .... 5·16 cm./sec.

Calculations similar to the preceding give for the mobility of a charged molecule of mercury methyl through hydrogen

0·33 cm./sec. if the attraction of the neighbouring molecules be neglected,

0·10 cm./sec. if this attraction be taken into consideration.

It is evident that the above considerations apply *à fortiori* to this particular case.

Experiments with regard to the Stability of the Vapour Ions.

The results described in the preceding section suggest that the ions formed from the large vapour molecules are unstable in the presence of the hydrogen molecules, inasmuch as the charge appears to be immediately transferred to the molecules of hydrogen. Experiments were then conducted to ascertain whether the vapour molecules could hold the ionic charge for any considerable period in the presence of hydrogen. For this purpose the chamber was exhausted by the mercury pump to a low pressure, and then methyl iodide was passed in and swept through by means of a water pump till the pressure was 7 cm. The ionic mobilities were then ascertained and a small quantity of hydrogen was added ; the mobilities were again determined ; further hydrogen was added, and so on till atmospheric pressure was reached. The chamber was again exhausted and a similar series of experiments was gone through, commencing with 51 mm. of methyl iodide. The mobilities were also measured in a similar manner when the initial pressures of the methyl iodide were 25 mm., 12 mm., and 6 mm. The results obtained are given in the following table :—

Pressure.			k_+.	k_-.
CH$_3$I.	H$_2$.	Total.		
mm.	mm.	mm.	cm./sec.	cm./sec.
70	—	70	2·67	2·67
70	59	129	2·52	2·52
70	183	253	2·18	2·18
70	315	385	2·06	2·06
70	687	757	2·00	2·00
51	—	51	3·95	3·95
51	16	67	3·80	3·80
51	61	112	3·51	3·61
51	334	385	3·00	3·12
51	714	765	2·65	2·75
25	—	25	7·51	7·55
25	85	110	5·90	6·03
25	360	385	4·00	4·20
25	732	757	3·50	3·85
12	373	385	5·95	6·41
12	751	763	4·45	5·62
6	379	385	9·50	—
6	757	763	5·20	6·81

The results for the positive mobilities are exhibited in the curves shown in fig. 8; the curve for pure hydrogen is based on Zeleny's values, and several points on the curve for pure methyl iodide have been calculated on the assumption of the validity of the law $pk = $ constant.

In order to interpret the results, let us consider the particular curve corresponding to 7 cm. of methyl iodide. It is evident that the addition of a small quantity of hydrogen does not appreciably alter the mobility; had the vapour ions been unstable and transferred their charge to the hydrogen molecules we would have expected a marked increase in mobility due to the small mass of the new carrier. When further hydrogen is added the mobility decreases only very slightly; in fact, although the pressure changes from 7 to 76 cm. the mobility only decreases from 2·7 cm./sec. to 2 cm./sec. From this result we deduce that as hydrogen is added to the methyl iodide the charge tends more and more to be carried as a hydrogen ion, although the methyl iodide molecule can accompany the charge to quite an appreciable extent even in the presence of a considerable quantity of hydrogen.

From an inspection of the curves it can also be seen that the mobilities approximate more quickly to those of pure hydrogen the smaller the initial quantity of methyl iodide.

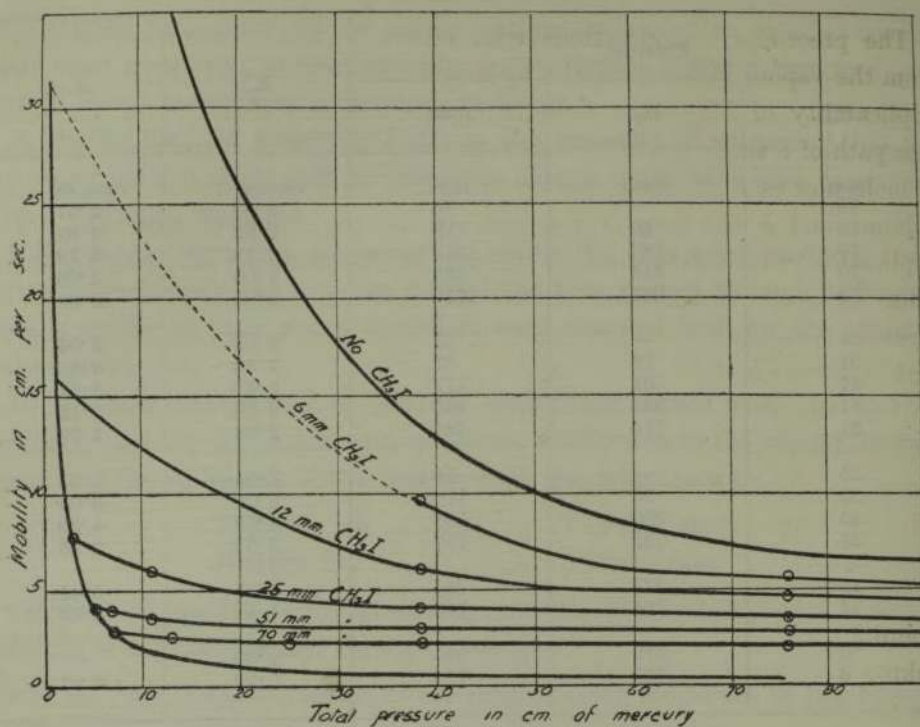Considerations of a similar kind apply to the negative ions.

Fig. 8.

Another set of mobility values was obtained in which ethyl bromide was used in place of methyl iodide; the resulting curves were of a similar nature to those above described.

Discussion on the Mechanism involved in the Transference of the Positive Charge.

It has been shown in the preceding sections that a positively charged vapour molecule when moving through hydrogen can transfer its charge to a hydrogen molecule. It is interesting to speculate on the different ways in which this might occur. On the one hand it is possible that, owing to the strong electric field surrounding the charged vapour molecule, a corpuscle might be dragged out of a hydrogen molecule; in this way the vapour molecule would become neutral, and the residual portion of the hydrogen molecule would on the ordinarily accepted theory carry a positive charge. On the other hand, the vapour molecule might transfer a positive unit of electricity to the molecule of hydrogen in a manner similar to what we may consider occurs in the case of the negative ion. The writer is more inclined to the latter view, especially as such a view appears to be necessary in order to explain the fact that in some gases, *e.g.*, sulphur dioxide, the positive mobility is greater than that of the negative.

The preceding considerations with regard to the transference of charge from the vapour molecule to the hydrogen molecule depend ultimately on the applicability of Maxwell's formula $L = \{\pi n \sigma^2 \sqrt{1 + M/m}\}^{-1}$ for the mean free path of a single uncharged molecule of mass M in a medium consisting of molecules each of mass m, n denoting the number of molecules per unit volume, and σ the sum of the radii of the two kinds of molecules. The application of this expression to the case of the diffusion of gases has been made by O. Meyer,* who calculated the diffusion coefficients for a series of gases by a method involving this formula, and obtained a striking agreement with observation.

If L denote the mean free path of the methyl iodide molecule through hydrogen at any pressure, and l the mean free path of the methyl iodide molecule through methyl iodide at this pressure, and if we regard the above formula as valid we deduce

$$\frac{L}{l} = \tfrac{2}{3} \frac{s'^2}{(s+s')^2},$$

where $\tfrac{1}{2} s'$ and $\tfrac{1}{2} s$ denote the radii of the vapour and gas molecule respectively. Taking as before $s'/s = 1\cdot34$, we obtain $L/l = 0\cdot22$ approximately. Now, the mobility at constant temperature is proportional to the mean free path, provided the ion is unaltered in mass and dimensions, as is readily seen from Langevin's expression for the mobility: $k = eL/MV$, where M denotes the mass of the ion, L its mean free path through the gas, and V its mean velocity of thermal agitation. It follows, therefore, that if the ion formed in pure methyl iodide at any pressure be unaltered or increased in mass and dimensions by the addition of any quantity of hydrogen, the curves for the mobilities shown in fig. 8 would all lie nearer the axes than the mobility curve for pure methyl iodide. The actual positions of these curves as determined experimentally imply that the ion diminishes in mass and dimensions as the hydrogen is added. If the ion is then to be regarded as consisting of a cluster of molecules, it is necessary to postulate the original transference of charge by either of the methods indicated above and, in addition, the decrease of the ion in mass and dimensions as the hydrogen is added; this might possibly arise if we regard the addition of hydrogen as decreasing the time during which the ionic cluster involves a methyl iodide molecule, so that when a considerable quantity of hydrogen is present the ion would be approximately a cluster of hydrogen molecules. Another explanation as to the nature of the passage of the electricity through the medium is given in the next paragraph; this view is capable of explaining in a simple manner all the preceding results and, moreover, is in harmony with other

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* 'Kinetic Theory of Gases,' 2nd Edition (English), p. 274.

phenomena in connection with gaseous ionisation, *e.g.*, the formation of fresh ions by collision.

The Mechanism underlying the Passage of Electricity through Gases at Ordinary Temperatures and Pressures.

It has been shown above that it is necessary either to postulate the existence of a unit of positive electricity or to suppose that there is some mechanism not involving the supposition of a positive electron by which a charged molecule can transfer its charge to a neutral molecule. Either alternative renders it extremely probable that when the ions move through a medium consisting of a mixture of two gases there is a continual interchange of charges between the two sorts of molecules ; the charge is associated for a fraction of its life in the gas with the molecules of one kind and for the remaining portion with the other kind of molecules. It is a natural inference to conclude that a similar process occurs in the simple gases such as oxygen, carbon dioxide, etc. In the previous paper it was shown that the observed mobility values of the gaseous ions could be explained approximately on the supposition that the ion consisted of a single charged molecule if we took into account the diminution of the mean free path due to the attraction of the molecules by the charge on the ion. This interchange of charge between the molecules in the medium occurs both for the positive and negative ions ; the marked differences in the values of the mobilities of the two kinds of ions in certain gases, *e.g.*, oxygen, hydrogen, etc., is explicable if we suppose that the charge which is in general associated with the molecule can exist in the free state for a certain fraction of its life. On this view the negative mobility would be greater than the positive for those gases whose molecules have a greater affinity for the positive charge than for the negative ; thus for gases such as oxygen and hydrogen it is necessary to suppose that the positive charge is associated with the molecules for a longer time than is the negative corpuscle. In addition it would appear from experiments on the mobilities in flames that the time during which the charge exists in the free state is a function of the temperature, so that as the temperature increases the ion approximates to a single detached electrical charge either positive or negative. Such a view harmonises with recent experiments by Moreau,[*] who found that in a flame at 2000° C. the mass of the negative carrier was $1 \cdot 1 \times 10^{-25}$ gramme, which is intermediate between that of a corpuscle (10^{-27}) and that of an atom of hydrogen (10^{-24}).

It follows also as a result of the experiments made with regard to the effect on the mobilities of small traces of vapours that we must suppose that

[*] 'Comptes Rendus,' vol. 148, p. 342, 1909.

the molecules of certain vapours (*e.g.*, water, alcohol, acetone) tend to hold the charge in association with them much more strongly than the molecules of the heavier vapours such as methyl iodide. Thus if a small quantity of water-vapour be mixed with carbon dioxide at one atmosphere the charge (both positive and negative) would be carried for a considerable portion of the path by the water molecules; owing to the relatively small mass of the molecule of water we would expect an increase in the mobility of the positive ion, but in the case of the negative ion this increase might be more than counteracted by the shortening of the period during which the corpuscle exists in the free state, so that on the whole the mobility of the negative ion would be decreased. Similar reasoning would explain, although merely descriptively, all the observed phenomena with regard to the effect of small quantities of vapours on the mobilities of gaseous ions.

It is of interest to record that Prof. Sir J. J. Thomson* has recently advanced the theory that the act of ionisation consists in the expulsion from the molecule of both a positive and a negative unit of electricity; such a view is quite in accordance with all the experimental results described in this paper.

I take this opportunity of expressing my gratitude to Sir J. J. Thomson for the inspiring interest he has manifested throughout the research and for many valuable suggestions.

* 'Phil. Mag.,' vol. 16, p. 685, 1908.