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XIX. *Further Experiments on Positive Rays.*

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[Plate IX.]

THE experience gained in the course of the investigations of these rays has led to some modifications in the apparatus which increase the brightness of the positive rays and thereby facilitate their investigation. The following are the most important changes made since the publication of my paper "On a New Method of Chemical Analysis," Proc. Roy. Inst. 1911.

Shape of the front of the Cathode and its position in the Tube.—Cathodes of various shapes have been tried—flat, concave, and convex; the best results have been obtained with a cathode shaped so that its section has the form represented by C in fig. 1 (p. 210).

The tubes we use for the discharge are spherical flasks about 30 cm. in diameter, the cathode being in the neck of the flask. The brightness of the rays is very much affected by the extent to which the cathode projects into the flask; if the cathode either extends far into the flask or is far back in the neck, the rays are comparatively feeble: the best position is when the front of the cathode comes nearly flush with the opening into the flask. The

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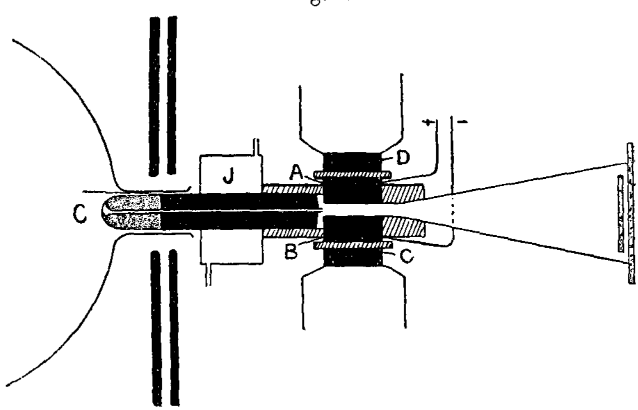
space between the sides of the cathode and the neck of the flask must be small, otherwise when monatomic gases such as helium or argon are used there is a considerable deposition of metal on the neck of the flask ; the discharge then tends to start from this deposit instead of from the cathode, and very few positive rays pass down through the hole in the cathode.

For the channel through the cathode we generally use fine copper tubes drawn out until the opening is sufficiently reduced ; the length of the tube is about 8 cm., and the diameters of the tubes we have used vary from ·1 to ·01 mm.

It is a matter of some difficulty to get the finest tubes sufficiently straight to allow a particle moving in a straight line to pass through the tube without striking against the sides. The following method was used when it was necessary to reduce the size of the tube as much as possible. Two flat pieces of steel were made as accurately plane as possible by the use of surface plates ; a shallow fine scratch was ruled on

Fig. 1.



one of the plates, and the two plates were then bolted together, the scratch making an exceedingly fine channel between the plates. With these very fine tubes it is necessary when taking photographs to give a very long exposure, 2 or 3 hours ; and to adopt special arrangements for keeping the magnetic and electric forces constant during this interval, as fluctuations in the intensity of these forces broaden the lines and neutralize the benefit derived from the smallness of the tube.

The photographic plates with which we have obtained the best results are the Imperial Sovereign. Inasmuch as the rays do not penetrate right through the film, the most suitable plates for these experiments might be expected to be those which had very thin films containing as much of the silver salts as possible. Guided by this consideration, I tried the old Daguerrotype silver plates treated with iodine, but did not obtain such good results as with the Sovereign plates.

For some experiments it is important that the magnetic and electric fields used to deflect the rays should be as co-terminous as possible, and so arranged that if necessary the length of these fields can be reduced to a few millimetres and the intensity increased sufficiently to give measurable deflexions. The arrangement represented in fig. 1, which was designed by Mr. Aston, has been found to give good results. The soft iron pole-pieces, which have flat plane ends A and B, are in an ebonite box which forms part of the observation-tube, the ends of the electromagnet CD fitting into recesses cut in the outside of the box. The flat ends of the pole-pieces, which are insulated, are used as the plates to produce the electric field. Care must be taken that the positive rays do not strike either ebonite or glass, as if they do they charge up the surface and produce an electric field which deflects the rays. Earth-connected pieces of tinfoil were placed on these insulators to prevent any charge of electricity accumulating upon them. A water-jacket J is placed round the observation-tube to prevent the wax getting hot and giving off vapour.

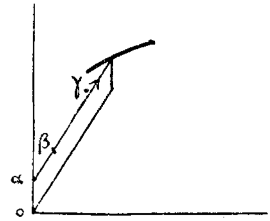
We shall now proceed to discuss some results obtained with this apparatus.

Secondary Lines on the Photographs of the Positive Rays.—These photographs show lines of two types: one type consists of a series of arcs of parabolas which, when the deflexion due to the electrostatic field is horizontal, start in most cases from points lying on a straight vertical line. Since the horizontal electrostatic deflexion is inversely proportional to the kinetic energy of the charged particles, this shows that the maximum kinetic energy possessed by the particles producing these lines is the same for each kind of particle.

These parabolic arcs are often of considerable length, indicating that there is a considerable range of velocities among the particles of the same kind. The ratios of the *latera recta* of the different parabolas are equal to the ratios of the values of e/m for the particles producing the parabolas, and are independent of the strength and distribution of the electric or magnetic fields. We attribute the formation of these parabolic arcs to particles which were charged before they entered the electric and magnetic fields, and which have retained their charges unaltered during their passage from one end of the field to the other. The value of e/m for the particle producing a line of this type can be determined at once by comparing the *latus rectum* of its parabola with that of a parabola due to a known particle, say the atom of hydrogen, or the mercury atom ; if the intensities of the electric and magnetic fields are known, we can determine the absolute value of e/m for any parabola without using any comparison lines. We shall call the lines of this type the primary lines.

When, however, the pressure of the gas traversed by the rays after passing through the cathode is not too low, there are other lines to be seen on the plate which have quite different properties from the primary lines (Pl. IX. fig. 2). They form curves of fairly uniform intensity which do not stop short at a finite distance from the vertical axis but are continued until they meet this axis : in some cases they pass through the origin itself, in others they start from points vertically above or below it. They are to be found on the side of the plate corresponding to negative charges as well as on that corresponding to positive. Their shape and also their position with respect to the primary lines depends upon the disposition as well as on the intensity of the electric and magnetic fields. If care is taken to make the electric and magnetic fields uniform and coterminous, the curves we are discussing become straight lines passing either through the origin or very near to it; examples of these are shown in figs. 3 and 11 (Pl. IX.). We see from the figure that though all the lines of this type pass nearly through the origin, one set actually passes through it, while another starts from a point on the vertical axis a little above it, the curves having the shape shown diagrammatically in fig. 4 *a*. Fig. 4 *b* (Pl. IX.) is a

Fig. 4 *a*.



photograph. A careful examination of the plate shows that the lower curve turns up abruptly towards its termination A and joins the upper one. There are sometimes several pairs of these lines on a plate running up into the primary parabolas due to particles having small atomic weights. The lines due to the heavier particles are often connected with lines corresponding to the lower curve in fig. 4 *a*, while for these heavy particles the upper curve is absent.

The separation of the lines in a pair such as is represented in fig. 4 *a* is much more pronounced when the magnetic field considerably overlaps the electric, and both are fairly uniform. Such a case is represented in fig. 5 (Pl. IX.), which is a reproduction of a photograph taken when the pressure in the observation-tube, *i. e.* the part of the tube between the cathode and the camera, was considerable. It will be noticed that these pairs occur on both sides of the vertical line through the origin, showing that this type of line is produced by negatively as well as by positively charged particles. An interesting point is well brought out by this plate: it will be noticed that there is no fogging of the plate between the two lines, while there is very considerable fogging of the plate below the lower line. In this case there is very little fogging above the upper line, but on other plates the part of the plate above the upper line is also fogged to some extent, though not so much as the part below the lower line; the space between the lines is in all cases free from fogging.

The straightness of the lines when the electric and magnetic fields are uniform shows that the rays which produce any one line must be moving with nearly the same velocity, the fineness of the lines showing that the variations in the velocity must be exceedingly small.

Origin of the Lines.—The lines of the type of the upper one in fig. 4 *a* are due, I think, to particles which passed out from the delivery-tube through the cathode uncharged, but which subsequently, by striking against a corpuscle, lost a corpuscle and became positively charged before they passed out of the reach of the electric and magnetic fields. The lower lines in fig. 4 *a* are due, I think, to particles which were charged when they passed through the delivery-tube in the cathode into the electric and magnetic fields, but which, by combining with a corpuscle, got neutralized before they escaped from these fields; the different points on the curve being due to particles which have gained or lost their charge at different points of their path. Let us consider the first type of secondary, and suppose that, as was the case in most of the experiments, the magnetic field slightly overlapped the electrostatic. In the curve fig. 4 *a* the initial vertical portion $O\alpha$ is due to the particles which acquired their charge after they had left the electric field, but before they had quite passed through the magnetic field, their vertical deflexion being due to the part of the magnetic field which stretches beyond the electric. The portions $\alpha\beta$ near α are due to particles which got their electric charge shortly before they left the electric field, while the portions $\beta\gamma$ further away from α are produced by particles which got charged at an earlier stage in their career.

Let us now consider the effect on the shape of the lines of a want of uniformity in the electric or magnetic fields. Since the lines are straight when the fields are uniform, the different particles which produce a line must all be moving with approximately the same velocity. Let this velocity be v, then if the particle acquired its charge at a distance ξ from the photographic plate, y the vertical displacement at the plate due to the magnetic field is given by the equation

$$y=\frac{e}{mv}\int_0^\xi x\mathrm{H}dx,$$

where H is the magnetic force at a distance x from the plate.

Thus
$$\frac{dy}{d\xi}=\frac{e}{mv}\xi\mathrm{H}_\xi,$$

where H_ξ is the value of H at ξ.

Similarly, if z is the horizontal displacement due to the electrostatic force,

$$z=\frac{e}{mv^2}\int_0^\xi x\mathrm{X}\,.\,dx,$$

where X is the value of the electrostatic force at a distance x from the photographic plate.

We have, therefore,

$$\frac{dz}{d\xi}=\frac{e}{mv^2}\xi\mathrm{X}_\xi,$$

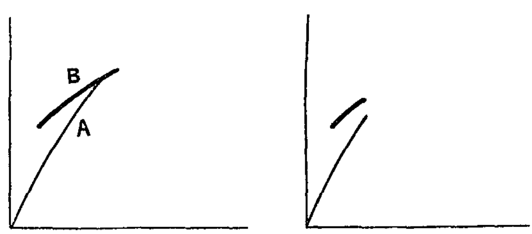
and so

$$\frac{dy}{dz}=v\frac{\mathrm{H}_\xi}{\mathrm{X}_\xi}.$$

And thus the tangent of the angle which the tangent to the curve makes with the horizontal represents the variations in the ratio of the magnetic to the electric forces. Take, for example, the case when the magnetic force extends beyond the plates used to produce the electric field and when the magnetic force gets weaker as we approach the cathode. The curve will start from the vertical line at some distance above the origin, and the curve will get flatter and flatter as we travel upwards from P ; in this respect it will resemble a parabola. This secondary curve must ultimately cut the primary curve corresponding to its particle at a point on the primary produced by a particle moving with the velocity v.

Considerable variations in the shape of the secondary curves may be produced by variations in the distribution of the electric and magnetic fields. Thus, suppose that the delivery-tube for the positive rays extends up to one end of the plates so that at this end there is no place where a charged particle is acted on by magnetic and not by electric forces. Then, if the electric and magnetic fields were coterminous at the other end, the shape of the secondary might be somewhat like that shown in fig. 6, the thick line representing the primary curve.

Fig. 6.

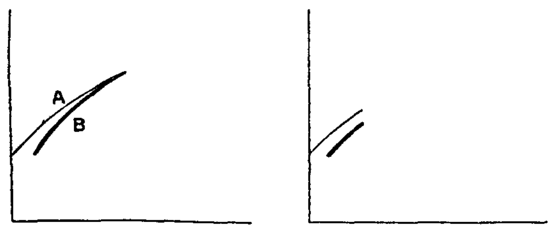


If, however, the magnetic field at the end next the camera overlapped to a considerable extent the electric field, then the secondary curve might resemble that shown in fig. 7, the secondary curve being now above the primary instead of below it as in fig. 6.

Thus, if the secondary curves were not completed on the plate, but stopped, for example, at AB (figs. 6 and 7), we might easily mistake the secondary line for a primary due to a particle which in fig. 7 had a value of e/m greater and in fig. 6 less than the primary to which it really corresponds. This is a point which requires careful attention when we use the curves produced by the positive rays to analyse the gases in the tube.

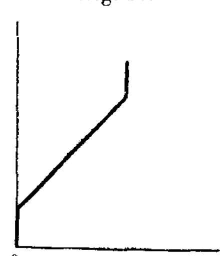
The two photographs reproduced in figs. 8 and 9 (Pl. IX.) show cases in which, by changing the disposition of the magnetic field, the secondary due to the hydrogen atom has been displaced from below its primary to above it.

Fig. 7.



If the delivery-tube for the positive rays did not reach up to the beginning of the plates used to produce the electrostatic deflexion, and the magnetic field overlapped the electrostatic at both ends, dy/dx would be infinite at the beginning and end of the curve, and the secondary curve would be shaped like the one shown in fig. 10.

Fig. 10.



An example of this is shown in the photograph reproduced in fig. 9 (Pl. IX.).

We see from these considerations that a secondary line may suffer considerable variation in position, and there is some danger, unless precautions are taken, that a secondary which has been displaced owing to some change in the distribution of the magnetic or electric fields, might be regarded as a line due to a different kind of particle. When the photographs of the positive rays are used to analyse the gases in the discharge-tube, the lines due to the primary rays are the only ones that can be relied on. The tests for these primary lines are (1) that they must be parabolic, and (2) that there should be a rapid increase in intensity in all these lines at places all situated on a vertical line (if the electrostatic deflexion is horizontal). The first condition is theoretically sufficient except with very special distributions of the electric and magnetic forces ; but I have found that in practice the secondaries are not infrequently very approximately parabolic when they are near to their primaries, so that unless a very high degree of accuracy were obtained in the measurement of these lines, their secondary nature might easily escape detection if this were the only test applied.

The secondaries we are now considering arise from the collision of neutral particles with corpuscles ; they cannot be produced by collision of the particles with other particles having a mass comparable with that of the neutral particles, for such a collision would deflect the path of the particles, and the lines in the photographs would become much more diffuse than is actually the case. The collisions which ionize the particles are between moving particles and corpuscles which are approximately at rest ; the effects of the collision will, however, only depend on the relative motion of the particle and corpuscle, and will be the same as if the particle were at rest and the corpuscle moving with the velocity of the particle. Now in order that a moving corpuscle may ionize an atom or molecule against which it strikes, the velocity of the corpuscle must exceed a definite limit which probably depends to some extent on the nature of the atom or molecule. Let us call this limit for a particular kind of atom V ; then in order that an uncharged atom of this kind should be ionized when it strikes a corpuscle at rest, it must move with a velocity greater than V : hence all the secondary rays formed by this atom must move with a velocity greater than V. There is thus an inferior limit to the velocity of the secondary rays due to a particular kind of atom or molecule. There is, however, a superior limit to the velocity of these rays as well as an inferior one. For these rays are due to particles which move with great velocity and which were uncharged when they entered the electric and magnetic fields ; they must, therefore, have been positively charged before passing through the cathode so as to be able to acquire this velocity, and then have become neutralized by combining with a negative corpuscle. The rapidly moving positively electrified particle must have attracted to itself and held bound a negative corpuscle ; it cannot, however, do this if the relative velocity of the two is greater than a certain limiting velocity. This velocity is determined by the condition that it is the velocity with which a corpuscle must be moving when it has sufficient kinetic energy just to carry it away from the attraction of the positively electrified particle. The work required to separate a corpuscle from a positively charged particle may be expected to be of the same order as that required to ionize the particle when neutral. Thus, if V is the velocity of the corpuscle when it can just ionize the particle; then, if the velocity of the particle were appreciably in excess of V, a positively charged particle would not get neutralized, while if the velocity of the neutral particle were appreciably below V it would not get ionized. Hence the velocity of the secondaries which arise in the way we are considering must be very approximately equal to V, a velocity which depends only on the nature of the particle, and not on the electromotive force applied to the discharge-tube. This accounts for the fact that although the primary line may be due to particles moving with a wide range of velocities, the particles in the secondary are all moving with the same velocity.

Energy required to Ionize a Gas.—By measuring, by the method described in former papers, the velocity of the particles forming the secondary rays corresponding to any atom, we can determine V the smallest velocity with which a corpuscle must move to ionize that atom. I find this velocity for the hydrogen atom to be about 2×10^8 cm./sec., a velocity which would be acquired by the fall of a corpuscle through a potential difference of 11 volts. Hence we may take 11 volts as the measure of the energy required to ionize an atom of hydrogen.

To give to the hydrogen atom the velocity 2×10^8 cm./sec. requires a potential difference of $11 \times 1{\cdot}78 \times 10^3$ (taking $e/m = 1{\cdot}78 \times 10^3$), or about 20,000 volts: to give the same velocity to an atom of oxygen would require $16 \times 20{,}000$ or 320,000 volts, a potential difference much greater than that which which we apply to our tubes. Hence we can see why the secondaries of the kind we are considering are only found with the lighter elements such as hydrogen and helium.

In addition to the secondaries which are due to the ionization of neutral atoms, there may be atoms which start with a positive charge and attract a corpuscle in their path through the electric and magnetic fields. When these fields are coterminous and uniform, these secondaries will, if the velocity is constant, be straight lines passing through the origin. If the fields are not coterminous the lines will be bent, and the bending will be complementary to that observed with the secondaries of the type previously considered. Thus, suppose the magnetic field overlaps the electric on the camera side of the observation-tube, then the rays which experience magnetic and not electric deflexions will be those which have previously travelled in their charged state all the electric and most of the magnetic field before reaching the critical region ; they will therefore have suffered a considerable deflexion, and the effect of the overlapping magnetic field will show itself in the most deflected portion of the rays, and not, as in the previous case, on the least deflected portion. Thus the curves for these rays will have the shape shown in the lower curve in fig. 4 *a* instead of that of the upper one in the same figure. If the velocities of the two kinds of rays were the same, we should have for each primary two secondaries of the kind shown in fig. 4 *a*. This disposition of secondaries is shown on many of the plates ; an example of it is given in fig. 12 (Pl. IX.).

This type of secondary, since it is produced by the combination of a positively charged particle with a negative corpuscle, might be expected to occur more readily with slowly moving particles than with fast ones : a particle moving faster than a certain velocity would not combine with a negative corpuscle, so that there would be a superior limit to the velocity of this type of secondary. There does not seem, however, any reason why there should be an inferior limit to the velocity, if the slow particles have retained their charge up to the time of entering the electric and magnetic fields ; and, as a matter of fact, this type of secondary often (as in fig. 5) shows itself as the edge of a patch of fogging on the plate rather than as a sharply defined line. There are however cases, notably with the mercury lines, where this type of secondary is more sharply defined than we should expect, and where there are, in the primary curves, particles with a smaller velocity than can be detected in the secondaries of this type.

In addition to the secondaries already mentioned, there are on many plates, for example that reproduced in fig. 14, prolongations of the primary which do not reach right up to the vertical axis but stop after going halfway. These prolongations of the primaries are parabolic and are continuations of the primary parabolas : they are therefore due to particles which in the deflecting fields have the same value of e/m as the particles which produce the primary parabolas.

The fact that the smallest electrostatic deflexion of the prolongation is just half that of the corresponding deflexion of the primary, shows that the swiftest of the particles in the prolongation has twice the kinetic energy of the swiftest in the primary ; and hence when in the electric field in the discharge-tube they have acquired twice the kinetic energy of the normal particles: they must therefore have had twice the normal charge when in the discharge-tube, but after they get into the deflecting fields the value of e/m must be normal. We infer from this that when in these fields the charge is normal; for though we should get the right value of e/m if both the charges and the masses were doubled, the double charge would for the same kinetic energy produce double the electrostatic deflexion, and therefore for a particle with twice the normal kinetic energy would give the normal deflexion: the actual electrostatic deflexion in the prolongation is, however, only half the normal deflexion. We conclude therefore that the prolongation is due to particles which had a double charge when in the discharge-tube, but which have lost one of their charges after having passed through the cathode.

The prolongations we are considering only occur with certain types of lines. Speaking generally, they are confined to lines due to atoms as distinct from those due to molecules; and moreover, when we find these prolongations we generally find on the same plate lines having a value of e/m twice that of the prolongations and beginning in the normal place ; these are due to the particles which have retained their double charge after passing through the cathode.

On the line due to mercury we find prolongations corresponding to particles which had three charges before passing through the cathode, and which have lost two of these charges after doing so ; the heads of these prolongations are only one-third the distance from the vertical of the normal heads. We find also on the plate lines due to mercury atoms with three charges which have retained these charges after passing through the cathode. The ability of the mercury atom to acquire multiple charges may be the reason why the parabola due to the mercury atom comes up much closer to the vertical than the parabolas due to other atoms. This is often very conspicuous : for example, the mercury line shown in Pl. IX. fig. 13 is parabolic, even when quite close to the origin.

Measurements of this curve show that some of the mercury atoms must have four or five times the kinetic energy possessed by the atoms of the other gases. It is possible that the heavy mercury atoms may linger longer in the charged state than the other atoms and last after the conductivity of the gas has become very small in consequence of the disappearance of the other atoms; then on the next break of the coil, these charged mercury atoms will be at first acted on by a much stronger electric field than that which exists when the resistance of the gas has been broken down and a considerable current passes through the tube.

On the Lines produced by the Negatively Charged Particles.—There are on the plates curves which, as the direction of the deflexions shows, are due to negatively charged particles. In one sense all these curves may be regarded as secondaries, for it is unlikely that the particles acquire their negative charges before passing through the cathode, as if they had done so they would have been retarded by the strong electric field which exists in front of the cathode. But though they are all, in this sense, secondaries, we find on examining the plates that the lines corresponding to the negatively charged particles may, like the positive ones, be divided into two types. Some of the negative lines, corresponding to the secondaries among the positives, come close up to the origin, while there are others which, like the primaries among the positives, are finite arcs of parabolas, terminating abruptly when they approach within a certain distance of the vertical axis. In fact these lines on the negative side are frequently exact reproductions in shape and size of the corresponding lines on the positive. An example of this is shown in fig. 14 (Pl. IX.), where the curves α, β are the lines corresponding respectively to the positively and negatively electrified atoms of oxygen. When the discharge passes through very pure oxygen, it will be seen that every detail in the positive curve is reproduced in the negative, including the prolongation of the parabola corresponding to the double charge. We see from this that even the fastest of the neutral oxygen atoms are able to attract and retain a negative corpuscle.

This identity in the shape of the positive and negative curves for the oxygen atoms might suggest the view that they are produced by a neutral molecule splitting up after it has passed through the cathode into a positive and a negative atom. We might be tempted to suppose that the negatively charged atoms in general arose from the dissociation of a molecule of a chemical compound in which the atom under consideration was negatively electrified, and was in combination with another positively electrified one: we might in fact suppose that we had something analogous to the dissociation of a molecule of an electrolyte in water.

Further consideration will show, however, that this view is not tenable, at any rate in a large number of cases. We find that the heads of the negative parabolas, like those of the positive, are arranged in a vertical line and that the distance of this line from the vertical line through the origin is the same as for the corresponding distance for the positive parabolas. It follows from this that the maximum value of $\frac{1}{2}mv^2/e$ is the same for the negative as for the positive particles, this quantity probably being the potential fall, V, between the negative glow and the cathode. Suppose now, to take an example, that the negatively charged hydrogen atom owed its charge to having been in chemical combination before it got through the cathode with an atom of carbon, the molecule of the compound being positively charged in the discharge-tube and acquiring a high velocity under the electric field ; after passing through the cathode the molecule gets neutralized, and then dissociates into a negatively charged hydrogen atom and a positively charged carbon one. The kinetic energy acquired by the molecule CH, if it had one charge of electricity, would be that corresponding to the fall through the potential V. Since the mass of the carbon atom is 12 times that of the hydrogen, the kinetic energy of the hydrogen atom will be that due to the fall of unit charge through a potential V/13 ; so that if this atom went through the same electric field on its way to the camera as a positively charged hydrogen atom which had been exposed in its atomic state to the electric field in the discharge-tube, it would suffer thirteen times the electrostatic deflexion of the positive one ; the photographs show, however, that they suffer the same deflexion. To explain the negative electrification of particles in this way, it would be necessary to suppose that the element with which they are combined before they are dissociated is one of very much smaller atomic weight. Hydrogen is the only element that would satisfy this condition ; and this explanation would not account for the negatively electrified particles of hydrogen itself, which are a very marked feature in the discharge. Again, if the negative electrification of oxygen were due to the dissociation of a hydrogen compound of oxygen, then for every negative oxygen atom we should have a positively electrified hydrogen one ; so that if the negative oxygen line were very strong, we should expect the positive hydrogen line to be strong also : the positives produced in this way would, however, be moving with much smaller velocities than those which had not been in combination and would therefore experience a much greater deflexion, which might be sufficient to drive them off the plate and prevent their detection. I have never been able to detect any increase in the brightness of the negative oxygen line when hydrogen was added to the gas; indeed, the brightest negative oxygen lines I ever observed were in an exceptionally pure specimen of oxygen. It is certainly true that in some compounds of oxygen the negative lines are much more pronounced than in others. I am inclined to think that the exceptional brightness of the lines is due to the presence of the hydroxyl radicle, and that the bright lines are due to OH and not to O.

The theory which on the whole seems to me most in accordance with the observations, is that the negatively electrified particles are due to systems which are positively charged when they are in the discharge-tube; then, after passing through the cathode, get neutralized by combining with a corpuscle, and when in the neutral condition have so strong an affinity for a negatively charged corpuscle that, in spite of the high velocity with which they are moving past it, they are able to capture a corpuscle and thus become negatively electrified. This attraction for the negative corpuscle depends on the chemical properties of the atom. The atoms of some elements do not exert sufficient attraction to enable them to become charged in this way: for example, I have never observed any indications of negatively charged helium, argon, nitrogen, or mercury, however strong the lines corresponding to the positively charged atoms may have been. On the other hand, the atoms of hydrogen, carbon, oxygen, sulphur, chlorine are conspicuous for the readiness with which under ordinary conditions they acquire a negative charge. The case of oxygen is especially interesting. In very pure oxygen, carefully dried by liquid air, the oxygen occurs on the negative side solely in the atomic condition: an example of this is shown in fig. 14, where the only line on the negative side is one due to atomic oxygen. If, however, a small quantity of hydrogen, say from 1 to 3 per cent. by volume, is added to the oxygen, another line appears on the negative side with a value of m/e about 33 times that for the hydrogen atom; an example of this line is shown in fig. 15 (Pl. IX.).

It is remarkable that this line disappears again when the quantity of hydrogen is increased, with 20 per cent. hydrogen it is no longer visible. I have a series of about 40 photographs of the discharge through mixtures of hydrogen and oxygen in varying proportions; in all of these, where the quantity of hydrogen is small, the line is visible, but unless the oxygen is greatly in excess it is invariably absent. I ascribe this line to the formation of H_2O_2. The question whether the actual carrier of the negative electricity is the molecule H_2O_2, or HO_2, or even O_2, is difficult to determine, as the lines are not strong enough to allow of the very finest tubes through the cathode being used. The following are the values of m/e obtained for this line on different plates, the value of m/e for the hydrogen atom being taken as unity:—33·5, 35, 33, 35, 32, 33, 33·5, 34, 35, 33, 32, 31; mean 33·3. This suggests that the carrier of the negative charge is not O_2 but either HO_2 or H_2O_2. The stronger negative line, with a value of m/e near 16, is, I am inclined to think, when hydrogen is present, not O but OH, as the measurements of this line on plates, taken with mixtures of oxygen and hydrogen, uniformly gave values of m/e slightly greater than 16. If the hydroxyl radicle is the carrier for this line, we can understand why the line is especially bright when the discharge passes through the vapours of some organic compounds, such as methyl alcohol, when the hydroxyl radicle is very likely to be liberated in the process of ionization. Though the line 33 only appears in mixtures of hydrogen and oxygen when the oxygen is greatly in excess; it appears in mixtures of ethylene and oxygen even when only a small quantity of oxygen is present.

The negative lines which appear when the discharge passes through the vapours of hydrocarbons are interesting. When there are no bonds between two atoms of carbon, as for instance in marsh gas, carbon monoxide, or carbon dioxide, the only line on the negative side which can be ascribed to carbon is the line for which m/e is 12, which is in general very bright. When, however, we take compounds in which there are bonds between the carbon atoms, such as ethylene and acetylene, we frequently find that in addition to the line for which $m/e=12$ there is another for which m/e is about 24, showing that we have a system with a strong affinity for negative electricity formed from two carbon atoms, with perhaps one or two atoms of hydrogen. When the discharge passes through benzene vapour we get in addition to the lines 12 and 24 a line near to 36; and I have sometimes thought that I could detect one near 48, though this is exceedingly faint: thus we can get strongly electronegative radicles containing three or more atoms of carbon. In very carefully purified helium the negative lines due to impurities are exceedingly faint, much fainter than they are in other gases. On one or two plates I have observed a negative line for which m/e was about 22.

On the way the Positive Rays are produced.—One very remarkable feature of the photographs is the length of some of the arcs of the parabolas, the horizontal deflexion of the end of the arc being often a large multiple of that of the beginning. Since the kinetic energy possessed by the particle is inversely proportional to its horizontal deflexion, this result shows that the kinetic energies of particles having the same value of e/m vary within wide limits. Assuming that the kinetic energy of the particle is due to the action upon it when in the dark space of the electric field, we might get this variation in the kinetic energy :—

1. If the charged particles all started from the same region, the end of the dark space, but before reaching the cathode got neutralized and so were only under the action of the electric field for a fraction of the journey through the dark space.
2. If the ionization which produced the positive rays occurred not merely at the end of the dark space, but to some extent throughout the whole of this space.
3. That the small amount of kinetic energy possessed by some of the particles is due to their colliding with the molecules of the gas whilst passing through this space, and in this way losing some of their kinetic energy.

Let us begin with the first of these suggestions. We know by direct experiment that unless the pressure is very low the rays after they pass through the cathode get neutralized and lose their charge for a time, sometimes acquiring it again by being ionized by the collisions they make. If this process went on in front of the cathode as well as as behind it, we should get variation in the kinetic energy of the positive rays, as some of them would have passed a larger fraction of their time than others in the uncharged state, when in the electric field. I do not think that this explanation is the true one, for the reason that the conditions in the dark space differ essentially from those which prevail after the particles have passed the cathode ; there is no electrical field after passing the cathode, so that the relative velocity of the positive rays and the corpuscles with which they are to combine is merely the velocity of the positive rays themselves. In the dark space in front of the cathode there is an intense electric field in which the corpuscles are moving far faster than the positive rays, so that the relative velocity of the positive rays and the corpuscles is very much greater than on the other side of the cathode. Thus the union of a positive ray and a negative corpuscle is far less likely to occur in the dark space than when the positive ray has passed through the cathode.

The third suggestion, that the loss of kinetic energy is due to collisions between the positive rays and the molecules through which they are moving in the discharge-tube, is open to the objection that it would produce effects of the same general character on all the lines on the plate. As a matter of fact, however, we find that some of the lines, notably those of compounds formed by the action of the electric discharge when it passes through mixed gases, are quite short, showing that all the rays have much the same kinetic energy. On the other hand, many of the lines are long and of nearly equal intensity along the whole of their length; while frequently abrupt alternations of intensity occur along the lines, giving them a beaded appearance. It is remarkable that this beading may occur on some lines, while other lines on the same plate are free from it.

The second explanation seems to me to be the most probable one, viz., that the positive rays are produced at different places in the dark space, and so fall through different potential differences and acquire different velocities.

One of the most striking things brought to light by the photographs is the extent to which the molecules of the gas filling the tube are broken up by the electric discharge. The dissociation which occurs in the gas is far greater than that required to make the gas a conductor of electricity; for all that would be required for this purpose would be for some of the molecules to lose a corpuscle and thus become positively charged: these would be able to carry the positive electricity, while the negative could be carried by the corpuscles or by molecules on which corpuscles had settled; a process of this kind would not involve the disintegration of molecules into atoms. The photographs show, however, that something much more complicated than this goes on in the dark space and the negative glow, for on all the photographs there are lines indicating atoms as well as those corresponding to molecules, and instead of there being only one type of carrier for the positive electricity, there are in general a considerable number of types, for example in benzene vapour I have counted seventeen different types of positive carriers.

Indeed, the splitting up of the gas by the electric discharge is so complete that the photographs of the positive rays obtained from the vapours of different hydrocarbons may be almost identical. Thus, for example, the prominent lines for the vapours of methyl alcohol, ethyl alcohol, ether $(C_2H_5)_2O$, and dimethyl ether are identical, showing that the more important rays are due to the products of dissociation of the molecules of these substances, and not to the undissociated molecules; the lines due to the latter, if they occur at all, are exceedingly faint.

On the Relative Brightness of the Lines on the photographic plate as an index of the number of the Carriers producing the Lines.—It is necessary, however, to be very careful in drawing any conclusion as to the number of carriers having any particular value of e/m from the brightness of the parabola corresponding to this value of e/m. When the kinetic energy of the particles of different kinds is the same, the photographic plate is much more sensitive to the lighter carriers with a high velocity than to the slower and heavier carriers. I had suspected that this was the case for some time, but had no idea that the effect was so marked until I compared the indications of the plate with those of a Faraday cylinder.

The details of the apparatus used for the Faraday cylinder will be described later: it will be sufficient to say here that they were such that the particles forming the different parabolas could be driven in succession into the Faraday cylinder, and the charges they communicated to it in a given time measured. As these charges (when the particles only carry one unit charge) are proportional to the number of particles entering the cylinder, the indications of the Faraday cylinder will give the number of the different kinds of particles. For example, when the gas in the discharge-tube was the residual gas left after the air was pumped out, the lines on the photographic plate due to the hydrogen atom and the molecule were very much brighter than that due to the oxygen atom, and the line due to the hydrogen atom than that due to the molecule. The experiment with the Faraday cylinder showed, however, that there were many more atoms of oxygen than of hydrogen, and also that there were more hydrogen molecules than atoms. Again, when the tube contained pure oxygen the line on the plate due to the oxygen atom was brighter than that due to the oxygen molecule ; the Faraday cylinder showed, however, that there were many more molecules than atoms carrying the discharge. In all cases, it is the lighter atoms which produce an effect on the photographic plate greater than is warranted by their number. I think the explanation is that these particles only penetrate a very short distance into the film, and so can affect only a very small amount of silver, the faster particles penetrate more deeply into the film than the slower ones ; there is thus more silver at the disposal of the quick particles; in other words, the film is more sensitive to quick particles than to slow ones.

The discrepancy between the number of rays of a particular kind and the intensity of the effects they produce is even more marked in the phosphorescence they excite in a willemite screen than the impression they produce on a photographic plate. With a willemite screen I have found that the brightness of the line due to the hydrogen atom may be very much greater than that due to the oxygen molecule when the Faraday cylinder method showed that there were 300 times as many positively charged molecules of oxygen as there were atoms of hydrogen. I think we may get an explanation of this, if we consider the mechanism by which ionization may be imagined to be produced. When a molecule is ionized by a negative corpuscle, the corpuscle has to possess a finite amount of energy. Let us suppose for the sake of clearness that the energy required is that due to a fall of the atomic charge through 10 volts; this corresponds to a velocity of the corpuscle of $1{\cdot}9 \times 10^{8}$ cm./sec., and we may suppose that to enable a corpuscle to escape unattended from a neutral atom, it must have a velocity of this order. If this velocity is to be communicated to it by collision with another body, that body must be moving with a velocity comparable with that acquired by the corpuscle.

Now in the case of the positive rays it is only in general the lightest atoms and molecules, the atom and molecule of hydrogen and the atom of helium, which possess velocities as high as this, and it is therefore only these rays which can produce ionization of the type of that produced by cathode particles. The heavier particles, though possessing far greater energy than that due to a fall through 10 volts, are moving much too slowly to impart by collision to a particle a velocity as great as $1{\cdot}9 \times 10^{-8}$ cm./sec. By sending these heavy particles between parallel plates maintained at different potentials and measuring the current sent across the plates, I have found that these heavy particles can produce a very considerable amount of ionization. The question arises, how is this ionization produced? The negatively electrified corpuscle must, in order to escape from the attraction by which it is bound to the atom, possess a certain amount of kinetic energy; this, if the mass is as small as that of a corpuscle, requires it to have a very high velocity. One method by which a comparatively slow positive ray might start off a corpuscle at a high speed is considered on p. 235 when we discuss the difference between ionization by cathode and positive rays. Again, if the corpuscle were firmly attached to a very much greater mass, this system could possess the requisite amount of energy with a very much smaller velocity, a velocity no greater than that possessed by the heavier positive rays, and which these rays could communicate to the system by colliding against it. This method of ionization might occur in a compound molecule if the negative charge clung, say, to an atom of oxygen, while it would not occur if the atoms were uncombined, when there would be no body of a mass comparable with that of an atom for the corpuscle to cling to. There are some phenomena which strongly suggest some process of this kind. For example, when the liquid alloy of sodium and potassium is bombarded by positive rays, it is only the specks of oxide on the surface which give out the sodium lines, the clean parts of the surface are quite dark. On the view just given this arises from the atom of oxygen being knocked off the atom of sodium with which it is combined and carrying off a negative charge, leaving the atom of sodium positively electrified, and in a condition to give out its spectrum: with the pure metal this process does not occur. There are some phenomena connected with the luminosity of flames which are also in accordance with this idea.

The great sensitiveness of willemite to cathode rays and to fast positive ones, and its inertness under the slower positive rays, would on this view be due to its luminosity being mainly produced by ionization of the type due to particles which have a velocity of the order 2×10^8 cm./sec.: velocities of this magnitude are possessed by the atoms of hydrogen and helium and the molecule of hydrogen, but not by the other atoms in an ordinary discharge-tube.

The fact that on the photographs the intensity of the lines due to particles of different kinds is not proportional to the number of particles which produce the lines, prevents us from drawing conclusions from the inspection of the photographs as to numbers of the various types of carriers of positive electricity present in the positive rays, and indeed would very often convey a wrong impression. Thus, for example, in a number of photographs I possess of the rays passing through mixtures of hydrogen and oxygen in varying proportions, the relative brightness of the lines of hydrogen and oxygen shows but little relation to the relative quantities of these gases present in the mixture. When, however, the numbers of particles in these lines were measured by directing them in succession on to the slit of a Faraday cylinder and measuring the charge received in a given time by the cylinder, it was found that the relative number of particles in the hydrogen and oxygen lines varied directly as the relative number of hydrogen and oxygen molecules present in the mixture.

The relative number of the different kinds of particles present in the positive rays is a quantity of fundamental importance for the consideration of the chemical changes which go on in the gas in the discharge-tube; this quantity is being measured in the Cavendish Laboratory by receiving the particles separately on a Faraday cylinder and measuring the charge received by the cylinder. The results of these measurements will be given in a separate paper.

Though the photographs do not give accurate quantitative estimates of the numbers of the different particles, they do give some very interesting results as to the processes at work in the ionization of the gases. Thus on some photographs the line due to an atom of, say, hydrogen was stronger than that due to the molecule, while on others the line due to the molecule was the stronger. Another interesting and in my opinion very suggestive result, comes to light from an inspection of the plates taken when the discharge passed through mixtures of hydrogen and oxygen. It is illustrated in figs. 17 & 18 (Pl. IX.) and also in figs. 21 *a*, 21 *b*. & 21 *c*. In the plates from which these figures were made there were very pronounced differences between the appearance of the lines due to the hydrogen atoms and those due to the hydrogen molecule. These differences may be of various kinds: for example, in fig. 17 the line due to the hydrogen atom is of uniform intensity throughout, while that due to the molecule is very weak at the head but intense elsewhere; in others the line due to the atom is uniform, but that due to the molecule is much more intense at some places than at others, thus having a beaded appearance. In others again (fig. 18) the line due to the atom is of uniform intensity, while that due to the molecule is very thin at the head and remains so for some distance, and then develops great intensity. The point, however, on which I wish to lay stress is that *when there are such differences between the lines due to the atom and molecule of hydrogen, there are similar differences between the lines due to the atom and molecule of oxygen.* In other words, that all the atomic lines have common characteristics, as have also all the molecular lines, but that these characteristics are frequently quite different. A similar effect can be observed in mixtures of hydrogen and nitrogen, and indeed in all the mixtures I have tried. As a general rule, the intensity along the lines corresponding to the atoms is more uniform than that along the lines corresponding to the molecules; the uniformity of the atomic line is especially marked in the lines corresponding to atoms with two charges, such as C_{++} N_{++} O_{++}. It is also noteworthy that on the lines corresponding to the monatomic elements helium and mercury we get a blending of the characteristic features of both the atomic and the molecular lines.

The difference between the atomic and the molecular lines suggests that the charged atoms and the charged molecules are produced by different processes ; that in fact there is more than one process of ionization at work, and that the process which produces the charged atom is different from that which produces the charged molecule. We have in the discharge-tube rapidly moving cathode particles moving away from the cathode, and positively electrified atoms and molecules moving towards it; each of these systems can, as is well known, produce ionization by collision. With regard to the ionization due to the cathode rays, there are several reasons for thinking that in the dark space itself this is not considerable. For if a cathode ray, starting from the cathode, produced on an average in its course through the dark space another corpuscle, this second corpuscle would, under the influence of the strong electric field which exists in that space, acquire a considerable velocity, though not of course so great a one as that of a particle which had started from the cathode and passed through the whole of the dark space. There would thus be a considerable range of velocity in the beam of cathode rays emerging from the dark space, and no approach to a condition where all the cathode rays in the bundle are moving with the same velocity. Now, although it is true that the cathode rays produced in a discharge-tube are not all moving with absolutely the same velocity, yet at the pressures at which these experiments on positive rays were made (of the order of 1/300 of a mm.), the variation in the velocities are not large, by far the larger portion of the particles having velocities which do not vary in value by more than a few per cent. So that we may conclude that the larger part of the positive ions which are produced by the cathode rays are produced beyond the dark space, and drift into this space under the action of the feeble electric forces which are found in the negative glow and the positive column.

We have data which confirm this idea. Glasson has shown (Phil. Mag. October 1911) that cathode rays with a velocity of $4 \cdot 7 \times 10^9$ cm./sec. moving through air at a pressure of 1 mm., produce 1·5 pairs of ions per cm. of path. These are comparatively slow cathode particles; in our experiments the velocity of the cathode particles when they left the dark space was considerably greater than this; and as the ionization due to cathode particles varies inversely as the square of the velocity, the ionization at the same pressure would be less than that found by Glasson. In our experiments, the pressure of the gas through which the particles passed was only about 3/1000 mm. Hence, if we left out of account the diminution in the ionization due to the increase in velocity, the cathode rays would only produce about 1·5 pairs of ions in a path of 333 cm. This distance is much greater than the width of the dark space. This confirms the conclusion that in the dark space itself the number of positive ions produced by the cathode particles, and therefore the number of positive rays arising in this way, would only be a small fraction of the number of cathode particles starting from the cathode.

Let us now consider the ionization due to the positive particles themselves. Direct measurements show that these, when they have passed through the cathode, produce ions at the rate of a pair of ions for a centimetre or so of their path through air at a pressure of 3/1000 mm.

Thus for the same number of rays the ionization due to positive ones would be greater than that due to cathodic ones: it is probable, however, that the cathode particles are much more numerous than the positive rays. For we know that when a positive ray strikes against a metal plate such as the cathode of a discharge-tube, the plate emits negative particles. Now the energy of a positive ray when it hits the cathode is very much greater than the energy required to liberate a negative particle; so that as far as energy is concerned the positive particle has ample store for liberating a considerable number of negative particles. We have indeed direct evidence that it actually does so; for Füchtbauer (*Phys. Zeit.* vii. p. 153) found that when positive rays, produced in a tube with a potential difference of about 20,000 volts between the anode and cathode, fell on a plate of aluminium, the number of cathode particles ejected from the plate was about four times that of the positive particles falling upon it. We should therefore expect the number of cathode particles starting from the cathode to be considerably greater than the number of positive particles arriving at it; this would imply that the greater part of the current through the tube is carried by the cathode particles. So that though the ionization produced by one cathode particle may be less than that due to one positive one, the excess of cathode particles over positive may make the total number of ions produced by the cathode particles comparable with that produced by the positive. In consequence, however, of the much greater speed of the negative corpuscles, their density will be less than that of the positive, so that there is at any time in the dark space an excess of positive electricity.

The positive rays have been shown by Füchtbauer (*loc. cit.*) and Austin (Phys. Review, xxii. p. 312) to be reflected to some extent when they strike against a plate of metal; *i. e.*, some of the rays rebound from the cathode without giving up their charge of electricity; after rebounding, they will be again attracted to the cathode by the electric field and have a second opportunity of communicating their charge to it. This rebound of the positive rays will increase the density of the positive electrification near the cathode, while it will diminish the current carried by the positive rays below the value calculated on the assumption that all the positive rays give up their charge to the cathode the first time they strike against it. The density of the positive electrification near the cathode will therefore be greater than the value deduced on the assumption that the current carried by the positive rays is equal to the density of the positive electricity multiplied by the velocity which a positive ion would acquire under the electric field in its journey from the place where it originated to the cathode. This I think may be the explanation of an important point to which Mr. F. W. Aston has called attention: this point is that, even if we suppose the whole of the current through the tube to be carried by the positive electricity (we have seen that probably only a fraction is), then the density of the positive electricity calculated on this assumption is far too small to be consistent with the equation

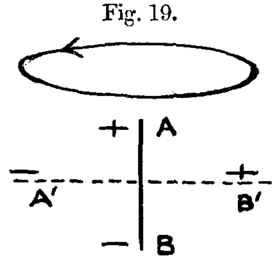
$$4\pi\rho = \frac{dX}{dx},$$

where ρ is the density and X the electric force in the neighbourhood of the cathode.

The reflexion of the positive rays involves the presence near the cathode of a number of positive ions with comparatively small velocities. As close to the cathode the cathode rays are also moving slowly, they would be able to combine with slowly moving positive particles, and thus give rise to the luminosity which is to be seen close to the cathode.

On the Difference in the kind of Ionization produced by Cathode Particles and by Positive Rays.—We have seen that on the photographs there are sometimes marked differences between the lines due to the atoms and those due to the molecules. This suggests that the atoms and the molecules get their charges in different ways. It seems, on *a priori* grounds, that we should ascribe the formation of the atoms mainly to ionization produced by positively charged atoms or molecules. For at the end of their paths in the cathode dark space these have in our experiments energy represented by the fall of the atomic charge of electricity through a potential difference of more than 20,000 volts. This is thousands of times the energy developed per molecule in any chemical reaction. It is therefore probable that when a charged particle of atomic mass collides with another atom, it will give to it sufficient energy to tear it from any compound, and therefore produce dissociation. We should expect therefore that the fast positive rays would disintegrate into atoms any molecules against which they struck. On the other hand, a fast cathode particle would be able to penetrate into the atom, and would collide rather with individual corpuscles than with the atom as a whole. We should expect then that in general the result of such a collision would be to detach a corpuscle from the molecule without necessarily splitting it up into atoms. The question arises, if the molecule were split into atoms by the impact of the positive rays, would these atoms be positively charged, or would when the atoms split off some be charged positively, others negatively? or, as a third alternative, would they be uncharged when liberated and acquire a positive charge by subsequently colliding with cathode rays? The evidence at present before us points to the conclusion that an overwhelming majority of these charged atoms have positive charges, *i. e.* have lost a corpuscle: has this corpuscle been detached by the impact with a positive particle which set the atom free? To force a corpuscle from an atom would seem to require the communication to the corpuscle of an amount of energy equivalent to that possessed by the corpuscle when it has a velocity comparable with 2×10^8 cm./sec. It is difficult to see how a comparatively slowly moving heavy atom could communicate so great a velocity to the corpuscle directly. It might, however, liberate a corpuscle which was previously moving with this velocity in a state of steady motion round a massive system. Take, for example, the following case: Suppose a corpuscle were moving in a state of steady motion round an electrical doublet A B, fig. 19, having a mass comparable with that of an atom;

Fig. 19.



suppose, now, that the doublet were struck by an atom and knocked into a position A′B′ at right angles to AB. The corpuscle would fly off with the velocity it had before the impact with the doublet: and it is easy to show that the work required to turn the doublet from AB to A′B′ is equal to the energy with which the corpuscle flies off. We see that in some such way as this a slowly moving atom with the requisite energy might detach a corpuscle from an atom.

Atoms with double charges.—The photographs show that the atoms of nearly all the elements, with the very suggestive exception of hydrogen, occur with two charges, though the number of these doubly charged atoms is always small compared with those having a single charge. We are able to detect the double charge on the atom because the parabola corresponding to the doubly charged atom is distinct from that due to the singly charged atom or molecule. We could not in this simple way detect the existence of doubly charged molecules, because the parabola corresponding to the doubly charged molecule would coincide with that due to the singly charged atom. We can, however, indirectly get some evidence on this point. Some of these doubly charged systems lose one of their charges before passing through the electric and magnetic fields: they are deflected by these fields into the parabola corresponding to the singly charged atom; but inasmuch as they had when in the electric field in the dark space a double charge, they will have acquired when in that field twice the kinetic energy of a singly charged atom. They will therefore occur on the parabola at a position which is only half the distance from the vertical line of that occupied by the atoms which have had a single charge during the whole of their career. The effect of this is to make the parabolic arc corresponding to the atom have a kind of beak. An example of this is shown in fig. 14 (Pl. IX.). Sometimes this prolongation of the parabola is of nearly uniform intensity, as in fig. 14; in other cases it is much brighter at the tip than at any other position, giving the curve a beaded appearance. Now it is remarkable that this prolongation of the parabolic arc towards the vertical axis occurs, as far as my experience goes, only on the lines corresponding to the atoms, and not on those corresponding to the molecules: this I think shows that the ions with double charges are atoms and not molecules. I have not observed on the plates any indications of molecules with two charges. Another question as to which we can get some information from the plates, is whether the doubly charged atoms get their double charge at one collision, or whether they get one charge at one collision, and the other at a subsequent one. If it took two collisions to give them the two charges, then we should expect that the number of these particles with an amount of energy approximately that due to the fall of the double charge through the whole of the dark space would be small compared with that of those which had a smaller amount of energy. For consider the condition which must exist for the particle to have the maximum kinetic energy: the two collisions which cause it must occur close together at the boundary of the dark space away from the cathode. Compare this with the region open for collisions which ionize the gas so that it falls into the cathode with about half this kinetic energy. Then, if the first collision occurs near the boundary of the dark space, a second collision near the cathode will be required, but the particle in this case is not obliged to make the first collision close to the boundary—it can go some way before making the first collision, and then make up for the loss of energy caused by the delay in making the first collision by making the second collision a little earlier. There is thus a much wider scope for adjustment in this case than in the previous one; and we should expect the number of particles with approximately half the maximum kinetic energy to be large compared with the number having nearly the maximum. As a matter of fact, however, the lines corresponding to the doubly charged atoms are conspicuous by the uniformity in their intensity. This is inconsistent with the ionization occurring in two stages; and we conclude that in some of the collisions which produce the charged ions the conditions are such that the ions receive a double charge.

Beading in the Molecular Lines.—We have seen that the possibility of double-charged ions gives a beaded appearance to the atomic lines, the beads appearing nearer the vertical line than the main portion. The molecular lines do not show this type of beading, but they show frequently another type in which the beads, instead of being nearer the vertical axis than the head of the parabola, are further away from it. A conspicuous example of this is shown in fig. 21 *b*, in which the larger quantity of the molecules of hydrogen and oxygen occur after the first beading. Sometimes, as in figs. 16 and 16 *a*, there are several sets of beads following each other at short intervals. The only atoms in which I have observed clear indications of this type of beading are those of the monatomic gases helium and mercury vapour, and for these gases there is no distinction between the atom and the molecule, so that this does not form an exception to the rule. This kind of beading depends very much on the position of the cathode in the discharge-tube and its shape. With some cathodes I have never observed them; with others I have found them when the cathode was in one position, not when it was in another. I think these are due to the impact of the cathode rays against the walls of the glass giving rise to slow secondary rays of great ionizing power. A slight inclination of the cathode might cause the rays to hit a portion of the discharge-tube which previously escaped, and thus start secondary rays nearer to the cathode, which would produce ions reaching the cathode with smaller energy than those which started from the negative glow.

It is remarkable that on many of the plates the head of the first beading on the molecular line is just twice the distance from the vertical of the head of the parabola, showing that the particles in the first beading have fallen through a potential difference just half of that fallen through by the particles at the head of the parabola. This is not, however, always the case; if it were, we should have to look for an explanation of this beading to some other cause than that just given. If, for example, aggregates of two molecules were formed possessing a single charge, and if, after passing through the cathode, the two molecules separated, one retaining the charge and the other going on uncharged, then the charged molecule would have half the energy due to a fall of the atomic charge through the electric field in the dark space, and would therefore be at the point often occupied by the first beading. If this were the explanation we should expect to find traces of the aggregates which had not broken up on passing through the cathode: these would be on a parabola corresponding to a value of e/m half that of the molecule. I have never been able to find traces of such parabolas. Again, it is not clear on this view why the existence of this beading should be so dependent on the shape of the cathode and its position in the discharge-tube. For this reason I am inclined to regard the ratio of 2 to 1 which sometimes exists between the horizontal distances of the first bead and the head of the parabola as accidental, and to prefer the first explanation of this beading.

Beading of the Mercury Line.—The beading on the mercury line is especially well marked since, as mercury is monatomic, the atomic as well as the molecular beadings occur on this line. As the mercury atom occurs with three charges, we get on the mercury line ($m/e=200$) beads corresponding to the atom which was highly charged when in the dark space, but lost two of the charges after passing through the cathode. As the kinetic energy acquired by the triply charged atom in the dark space is three times that acquired by the singly charged atom, the head of the bead corresponding to the triple charge will only be $\frac{1}{3}$ of the distance from the vertical of the head of the main portion of the parabola. This would bring the mercury parabola much nearer to the vertical and to the origin than the other parabolas. Now it is a very remarkable feature of the mercury parabola that it very often seems to reach right up to the origin, as, for example, in fig. 14. Measurements show that this is a parabola up to quite close to the origin: if this is so, then some of the particles must have acquired an amount of kinetic energy very large compared with that acquired by the fall of the atomic charge through the potential difference in the dark space. From the appearance of the curve a triple charge would hardly be sufficient to account for the close approach to the origin. Can it be that some of the mercury ions linger on from one discharge of the induction-coil until the next, and thus get exposed to the intense field which acts on the gas in the early stages before the normal discharge is established?

Besides the ionization due to the collisions with the positive and cathode particles, there must be some due to the "Entladungstrahlen" which are emitted from the negative glow as well as from the Röntgen rays which are produced when the cathode rays strike against the walls of the tube. At these low pressures there would be little absorption of such rays by the gas in the tube, so that the ionization due to this source would be uniform throughout the dark space. We are at present without the data which would enable us to estimate what proportion of the ionization is due to these rays and what to ionization by collision. The Röntgen rays, when they strike against the cathode, cause it to emit negative corpuscles. Now the experiments of Mr. Whiddington and others show that the velocity of the corpuscles ejected when Röntgen rays fall on a metal plate is approximately the same as the velocity of the cathode rays which produce them. If we apply this to the case of the discharge-tube, it indicates the existence of two streams of cathode particles, one due to the impact of the positive particles which emerge with comparatively small velocities (the experiments of Füchtbauer and myself indicate that this velocity is comparable with that acquired by the fall of a cathode particle through a potential difference of between 20 and 30 volts); and another stream due to the incidence of the Röntgen rays which emerge with a velocity comparable with that due to the potential difference between the anode and cathode in the discharge-tube, which amounts to many thousands of volts. The comparative homogeneity of the stream of cathode particles shows that the production of cathode particles by these two methods cannot be comparable in importance. Indeed, it would seem that any preponderating production of these particles by the second method would lead to instability in the discharge, for the ejected particle would start with a velocity comparable with that due to the whole electric field; it would in its course through the dark space increase this velocity; the Röntgen ray it produced at the end of its course would eject from the cathode cathode rays with a higher initial velocity than their parent, and the process would go on evidently leading to instability. If even an appreciable fraction of the cathode particles were ejected from the cathode by this method, we should expect to find in the cathode stream sets of cathode particles, α_1, α_2, α_3—moving more rapidly than the main body of these particles, and such that the energy possessed by an individual particle in the set α_2 exceeded that possessed by one in α_1 by the energy acquired by a cathode particle in falling through the dark space, while the energy of one in set α_3 exceeded that of one in α_2 by the same amount, though the number of particles in α_2 would be much smaller than that in α_1, and the number in α_3 still smaller than in α_2, and so on. As we have no evidence of the existence of a spectrum of this kind in the cathode rays, I think we must conclude that practically the whole of these rays are produced by the positive ions.

The smallness of the electric force at the end of the dark space is responsible, I think, for the luminosity in the negative glow, for when the field is strong, as in the dark space, the corpuscles and positively charged atoms and molecules acquire such great velocities that they rush past each other without combining. When, however, this field vanishes, positive and negative particles may only have small relative velocities and combine and give out light in the process. It is in the negative glow that we must look for new compounds formed by the union of atoms dissociated by the discharge.

Chemical Compounds produced by the Electric Discharge in Gases at very low Pressures.—The study of the positive rays has revealed the existence of some compounds which have not hitherto been detected by chemical methods. The measurement of m/e for the lines on the plate gives us the molecular weight of the carrier producing the line, or of some submultiple of it if the carrier is charged with more than one unit of electricity. In some cases this leads to the identification of the line without difficulty ; in other cases more than one kind of carrier might give the right molecular weight: for example, if we found a carrier having a molecular weight 28 it might be N_2, CO, or C_2H_4 : in such cases further experiments are necessary. If it was found, for example, that the line was absent when nitrogen had been very carefully eliminated from the gas, there would be a strong presumption that the line was due to the nitrogen molecule. By observing the behaviour of the line when the gas in the discharge-tube is varied, we can often determine without ambiguity the gas to which it is due.

I shall in what follows confine myself to the consideration of lines which satisfy both the tests for a primary line given on page 217. There are several lines satisfying the first of these tests which cannot be explained by any known substance; but as I do not feel sure that the possibility of their being secondaries is excluded by this test, I shall not base any conclusions upon them. There is a strong one corresponding to an atomic weight 6 in fig. 20 (Pl. IX.) taken with a mixture of helium and hydrogen.

Existence of H_3.—On several plates taken when the discharge-tube contains hydrogen, the existence of a primary line for which $m/e = 3$ has been detected. There can, I think, be little doubt that this line is due to H_3, and not to the carbon atom with four charges; for if it were due to carbon we should expect to find it conspicuous in carbon compounds, which it is not, and it would be accompanied by the lines due to the carbon atom with 1 and 2 charges, both of which are easily developed. These do not, however, accompany the line under consideration.

The line m/e does not occur, as far as we know, in absolutely pure hydrogen, but if a trace of air or oxygen is added to very pure hydrogen, the line appears under certain conditions of pressure and current.

Copies of photographs of plates showing this line are given in figs. 21 *a*, 21 *b*, and 21 *c* (Pl. IX.); the line is the one marked α; above it are the lines due to the hydrogen atom and molecule. The other lines on the plate are due to the oxygen atom and molecule and to the mercury atom. The existence of this substance is interesting from a chemical point of view, as it is not possible to reconcile its existence with the ordinary conceptions about valency, if hydrogen is regarded as always monovalent. The polymeric modification of hydrogen seems to require special conditions for its formation, for it cannot be detected on many of the plates taken with hydrogen in the tube.

Formation of N_3 *or* N_3H *by the Discharge.*—When the discharge passes through nitrogen at not too low a pressure, a strong line is found for which m/e is about 43, the numbers ranging from 42 to 44. This value of m/e is about the most embarrassing one there is for the application of this method of analysis, for there are many compounds which might occur in the tube which have values of m/e equal or nearly equal to 44. CO_2 for example, a common impurity in the tube, has a molecular weight 44 and would give a line in this region, and one test for the presence of CO_2, the existence along with it of CO, cannot be applied in the case of the discharge through nitrogen, as N_2 has the same molecular weight and would of course be present. N_2O has again the molecular weight 44, and might be formed if oxygen were present, and NO_2 has a molecular weight 46. We have, therefore, to apply further tests before we can identify this line. If the line were due to CO_2 present as an impurity, it is difficult to see why the presence of nitrogen should make the line so much stronger. Again, if it were due to CO_2, the oxygen lines would be found, as these are readily developed on both the positive and negative sides when oxygen, free or combined, is in the tube. But on some of the plates, when great care had been taken to get rid of oxygen, the line under consideration was strong while the oxygen lines were too faint to be detected. This is unfavourable to the view that the line is due to CO_2 or N_2O, and leaves us with N_3 and N_3H as alternatives. The hydrogen lines were present on all the plates, as, indeed, they always are, but I could not detect any increase in the intensity of the line under consideration when a considerable amount of hydrogen was mixed with the nitrogen. I am inclined, therefore, to regard the line as due to N_3 and not to N_3H. This line is not nearly so strong as the line due to the nitrogen atom, and, judging from the evidence afforded by these photographs, I should be inclined to attribute the "active form of nitrogen," investigated by Professor Strutt, to atomic nitrogen rather than to N_3. It is interesting to find that in the discharge-tube nitrogen exists in an exceptionally large number of modifications. N_{++}, N_{+}, N_{2+}, N_{3+} are found on all plates when the tube contains nitrogen, and on one or two plates I have found a line with $m/e=4{\cdot}7$, which I attribute to N_{+++}. I have never found a line corresponding to nitrogen with a negative charge.

On some Lines observed when the Discharge passes through mixtures of Hydrogen and Oxygen.—We have already alluded to the negative line in the neighbourhood of $m/e=32$ when the discharge passes through oxygen containing a small proportion of hydrogen. There is also a line on the positive side with a value of m/e about 50; its occurrence is not, as in the case of the negative line, limited to those mixtures which contain a small quantity of hydrogen; it occurs in all mixtures. I have not found it, however, in very pure oxygen. The most natural origin of the line would be ozone. Against this, however, is to be set the fact that it does not occur in pure oxygen; if it is not ozone, the alternative seems to be H_2O_3.

With mixtures of hydrogen and oxygen we get the water line, $m/e = 18$, and sometimes a faint line for which m/e is about 20; the compound H_4O would satisfy this condition.

With pure oxygen, or with a large excess of oxygen, the mercury lines disappear, owing I suppose to the combination of the oxygen and the mercury vapour. With new aluminium cathodes I have found that, whatever be the gas in the tube, the mercury lines are either absent or very faint; they attain, however, considerable strength after the tube has been used for some time and the electrodes have got saturated with mercury vapour.

When the discharge passed through CS_2, I found the line $m/e=44$ very strong; this, I think, is due to the new compound CS discovered by Sir James Dewar and Mr. H. O. Jones. Special precautions have to be taken in this case, as CO_2 gives the same line; oxygen was carefully excluded, without affecting the strength of the line, and in this case the line due to CO was exceedingly faint. This is a very searching test, as when CO_2 is in the tube, the line due to CO is always very strong, generally stronger than the one due to CO_2 itself.

The ammonia line was found when mixtures of nitrogen and hydrogen were in the discharge-tube.

It is quite possible for an element to be in the tube without producing its line on the photographic plate. Thus I made a number of experiments with nickel carbonyl in the discharge-tube with the object of determining the atomic weight of nickel by this method, but I was never able to detect a line corresponding to nickel *.

Again, when zinc ethyl is in the tube, I have never been able to detect the zinc line.

Indeed, with the exception of mercury vapour, the lines due to heavy molecules or atoms are not so conspicuous as we might expect. I attribute this to the peculiarities of the photographic plates, which seem much more sensitive to rapidly moving light atoms than to heavy ones with the same amount of energy but a smaller velocity.

As the photographic method, although excellent for detecting the existence of different substances in the discharge-tube, is not suitable for quantitative measurements of their

* Since this paper was communicated the nickel lines have been detected when a stream of nickel carbonyl ions keep running through the tube and the discharge is kept on for a short time with long intervals between the separate discharges.

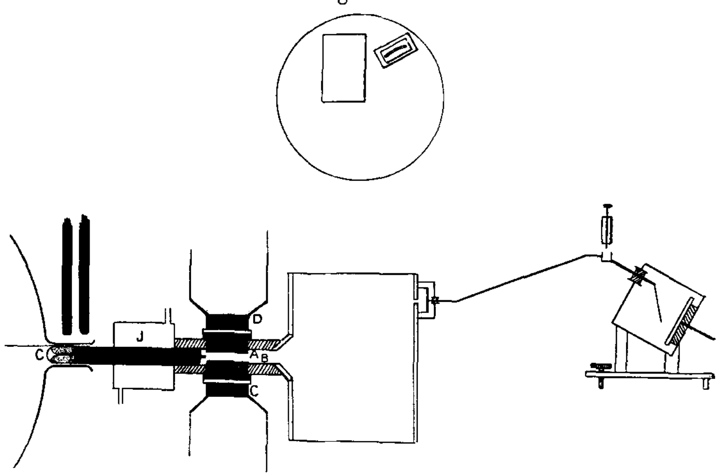
relative amounts, I have supplemented it by another method which enables us to measure the number of charged particles of any particular kind. The arrangement used for this purpose is represented in fig. 22. The particles, after passing through the electric and magnetic fields, fall upon the end of a closed cylindrical box, B. In the end of this box nearest the discharge-tube a parabolic slit 1 mm. in width is cut, the vertex of the parabola being the point where the undeflected rays would strike the end of the box, and the tangent to the vertex the line along which the particles would be deflected by the magnetic force alone. This slit is the only entry into the box. Thus all the particles which enter the box have the same value of e/m, and by altering the value of the magnetic field, one set of particles after another may be driven on to the slit and thus admitted into the box. Inside the box, and immediately behind the slit, there is an insulated long and narrow metal vessel placed so that every particle passing through the slit has to fall into this vessel. This vessel is connected with a Wilson tilted electroscope, so that the charge received by it can be measured.

At first considerable trouble was caused by the corpuscles which the metal around the slit emitted when it was struck by the positive rays ; to prevent these entering the Faraday vessel a permanent magnet was placed so as to produce a strong field between the slit and the Faraday vessel. This deflected the corpuscles away from the vessel without having any appreciable influence on the positive rays. A part of the front face of the vessel in which the Faraday cylinder was enclosed was cut away and a willemite screen inserted; by deflecting the positive rays on to this screen and observing the brightness of the parabolas, one could ascertain whether the conditions of the discharge-tube were such as to ensure a plentiful supply of positive rays. The face of the vessel, with the parabolic slit and phosphorescent screen, is represented in fig. 22.

The pressure in the observation tube was made as small as possible by the use of charcoal and liquid air ; the pressure in the part of the tube through which the discharge passed was generally about 3/1000 of a millimetre.

The Wilson electroscope gave a deflexion of about 100 divisions for a volt. The method of observation was as follows:—the positive rays were deflected by a constant electric field, and then the magnetic field was increased by small increments, and the deflexion of the Wilson electroscope in 10 seconds observed. Unless a parabola came on the slit there was practically no deflexion of the electroscope; as soon, however, as the magnetic force was such that a parabola came on the slit, there was a considerable deflexion, which vanished when the magnetic force was slightly increased so as to drive the parabola off the slit. The appearance and disappearance of the deflexion of the

Fig. 22.

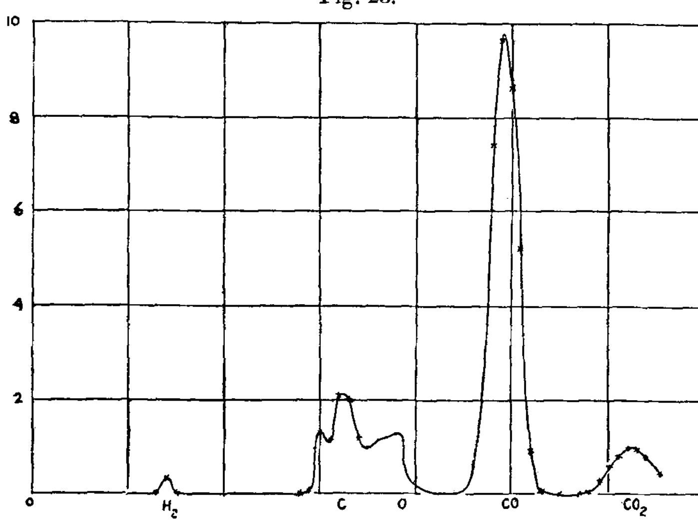


electroscope were surprisingly sharp, so that lines quite near each other could be detected and separated. With the first apparatus we tried, the power of separating the lines was not much inferior to the photographic method; and I believe that it is possible to improve the method by diminishing the width of the slit and making other improvements suggested by experience until it is more sensitive than the photographic method. It is in many ways more convenient as the tube has not to be continually opened to insert and remove the plates, it is more expeditious, and has the great advantage of being metrical. An example of the results obtained by this method is graphically represented in fig. 23. The abscissæ represent the magnetic force, the ordinates the deflexion of the electroscope in 10 seconds.

The gas in this case was carbon monoxide at a pressure of about 3/1000 of a millimetre. The nature of the particles producing the various peaks on the curve is indicated on the figure.

A comparison of this curve with a photograph of the discharge through the residual gas shows many interesting differences. On the photograph the strongest lines are those due to the hydrogen atom and molecule. The curve shows, on the other hand, that the number of hydrogen particles is only a small fraction of the number of CO particles. The extraordinary sensitiveness of the photographic plate for the hydrogen atom, in comparison with its sensitiveness to other atoms and molecules, is well brought out by this curve.

Fig. 23.



Carbon Monoxide, 320 Volts.

Another instance of the same effect is that when the discharge-tube is filled with mixtures of hydrogen and oxygen, the proportions of gases in the mixture may be altered within wide limits without producing any sensible effect on the relative brightness of the hydrogen and oxygen lines on the photograph. With the Faraday cylinder method, however, the magnitude of the effects found for the hydrogen and oxygen particles were roughly proportional to the amounts of these gases in the mixture. Examples for mixtures when the proportions by volume of the mixture were (1) 1 of H and 2 of O, and (2) 2 of H and 1 of O, are shown in figs. 24 and 25.

It will be noticed that in the mixture of hydrogen with two parts of oxygen, the number of charged oxygen molecules is greater than the number of charged atoms; while in the case of the mixture of two volumes of hydrogen to one of oxygen, the number of charged oxygen atoms appears to be greater than the number of charged oxygen molecules. This may possibly be due to a part of the peak ascribed to the oxygen atom being in reality due to molecules of water-vapour, the slit being hardly fine enough to separate values of m/e as close together as 16 and 18.

Fig. 24.

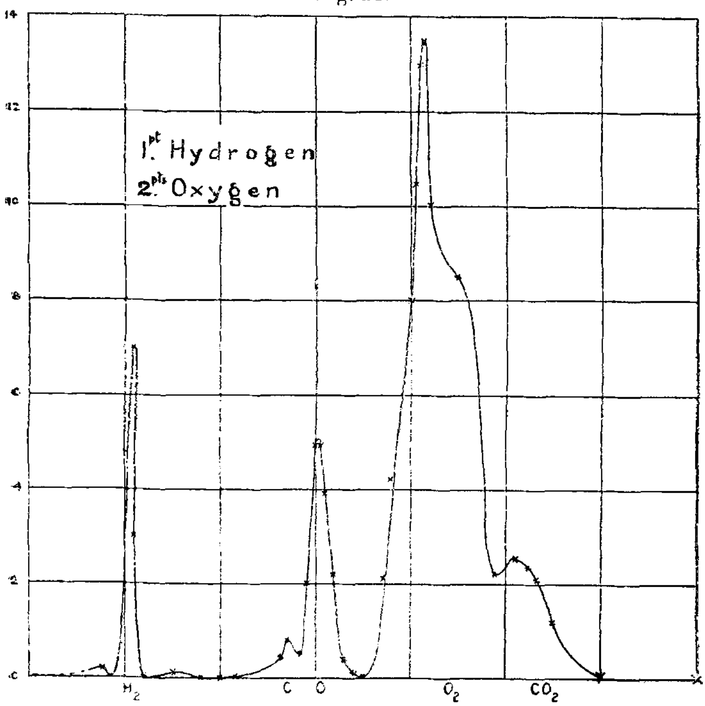
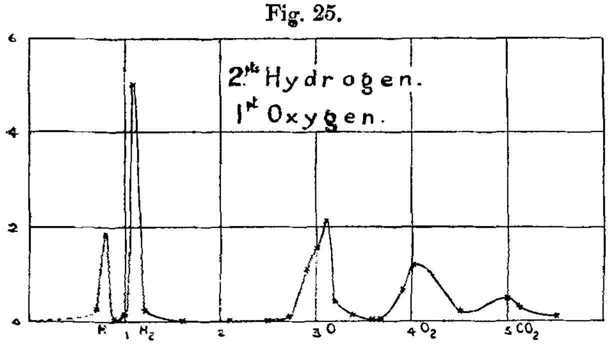


Fig. 25.



The negatively-charged hydrogen atoms seem to have the same preponderance in their effect on the photographic plate over other negative atoms as positive hydrogen has over other positive atoms. Thus on all the plates the line corresponding to the negative hydrogen atom is well marked, often comparable with the line due to the negative oxygen atom. With the Faraday cylinder method, the negative hydrogen atoms can only just be detected, while the negative oxygen ones produce large deflexions.

The discrepancy between the effects produced by hydrogen atoms and an equal number of heavy atoms is even more marked with a willemite screen than with a photographic plate: thus the willemite screen may show the hydrogen lines intensely bright, while the CO line is hardly visible, when measurements made with the Faraday cylinder show that the number of hydrogen particles is only a few per cent. of the number of CO particles. An interesting point and one that requires further investigation, is that with the heaviest particles of all, the mercury ones, the discrepancy between the results obtained with the Faraday cylinder and the photographic plate is not so great as it is with some of the lighter particles.

When the positive rays are detected by a phosphorescent screen or a photographic plate, we find that whatever gas may be in the discharge-tube, the hydrogen lines are strong; this suggests that in all gases there are a great number of positive carriers having the same mass as the atom of hydrogen. With the Faraday cylinder method, however, we find that the number of charged atoms of hydrogen is small unless hydrogen is introduced into the tube; this small quantity is not greater than that which might be accounted for by gas given out by the electrodes or liberated from the walls of the discharge-tube. The results obtained with the screen and plate are thus due to the abnormal sensitiveness of these agents to the rapidly moving hydrogen atoms, which makes them give a false estimate of the number of these atoms taking part in the discharge.

Are the atoms in the molecule of a gas charged one with positive the other with negative electricity?—It is a matter of fundamental importance to know if the atoms in the molecules of gases, compound or elementary, are charged with electricity or not. In a molecule of hydrogen, for example, is one atom positively, the other negatively, charged? In a molecule of hydrochloric acid gas, is the hydrogen positively, the chlorine negatively, charged? In a molecule of ammonia, has the nitrogen atom three negative charges and each of the hydrogen atoms one positive charge? It seems to me that we can get valuable information on this point by the study of the positive rays, now that, by the Faraday cylinder method, we can measure the number of positive rays of any kind taking part in the discharge. Let us take as an example the case of CO. If the carbon atom in this compound were positively charged, the oxygen atom negatively, then if a molecule of CO were split into atoms by the impact of a positive particle, the carbon atom would be positively electrified, the oxygen one negatively. The negatively electrified oxygen atom would move away from the cathode, and though it might after reaching the negative glow sometimes acquire a positive charge and be attracted to the cathode and become a positive ray, we should expect that the number doing so would be small compared with the number of carbon atoms which start with a positive charge. Thus, if the atoms in CO are charged we should expect to find in the positive rays produced when the discharge passes through CO, a much greater number of carbon atoms than of oxygen ones. I have investigated by the Faraday cylinder method the discharge through CO, the result is represented in fig. 23. It will be seen that the number of positively charged carbon atoms only exceeds that of the positively charged oxygen ones in the ratio of 11 to 7; and this number underestimates the number of oxygen atoms which came through the cathode, for some of these after getting through the cathode acquired a negative charge. Measurements by the Faraday cylinder showed that about 2/7 did so, while the number of carbon atoms acquiring a negative charge was insignificant in comparison. Taking the negative oxygen atoms into account as well as the positive, we find the proportion between the carbon atoms and the oxygen ones as 11 to 9; the numbers are so nearly equal as to preclude the atoms carrying opposite electrical charges when in the molecule.

Further evidence against the existence of these charges on the atoms is afforded by the consideration of the number of atoms in the positive rays which carry multiple charges. If the atoms in CH_4 or CO_2, for example, were charged, we should expect to find a considerable number of carbon atoms with four charges, whereas as a matter of fact no such atoms have been observed.

The view of the forces between the atoms in the molecule of a gas which is most in accordance with the behaviour of the positive rays, is that these forces are due to the atoms behaving somewhat after the manner of electrical doublets;

i. e., that the total charge on each atom forming a part of a gaseous molecule is zero, but that in each atom the positive and negative charges are so arranged that the force between adjacent atoms is attractive. I have not yet, however, tried any compound which is a strong electrolyte, it is possible that the atoms in such a compound might be charged.

There is, I think, other evidence besides that derived from positive rays in favour of the view that the atoms as a rule are not charged. For example, dissociation of gases at quite low temperatures (say 70° C.), such as takes place with nickel carbonyl, is not accompanied by any abnormal conductivity. And although, as I showed many years ago (Phil. Mag. [5] xxix. pp. 358–441), there is considerable conductivity at high temperatures in gases which dissociate at these temperatures, yet this conductivity seems to depend greatly on the contact of these gases with the hot metal of the electrodes between which the current is measured; suggesting that the charging up of the atoms in this case may be due to the electricity which we know to be emitted by hot metals. Quite recently Schmidt (*Ann. d. Phys.* xxxv. p. 401) has observed considerable conductivity at temperatures less than 200° C. in a vessel containing the vapour of cadmium iodide, obtained by heating the salt in the vessel in which the conductivity is observed. The cadmium iodide is dissociated, but we do not know whether the conductivity is due to cadmium iodide which has existed as vapour and then been dissociated, or whether it is due to systems which were dissociated when driven off from the salt by the heating. In the second case other considerations would come in, which can be illustrated by considering the case of electrolytes in solution, when the dissociation of the salt seems to be accompanied by the charging up of the atoms. If the atoms get charged in the electrolyte, it may be asked, why should they not get charged in the case of gases? The conditions are very dissimilar. We may regard the two atoms in the molecule as analogous to the two plates of a condenser, and the acquisition of a charge by the atoms as analogous to the charging up of the condenser. Now the work required to give a fixed charge to a condenser is inversely proportional to the capacity of the condenser, so that the smaller the capacity the greater is the amount of energy required to charge it. We should, however, expect that the capacity of a molecule when in the gaseous state would be much less than when it was in solution in a liquid of large specific inductive capacity; the specific inductive capacity would of itself increase the capacity, and in addition there would be the opportunity of the atoms in the molecule forming aggregates, thus becoming, from this point of view, much larger systems and having greatly increased capacity. The same considerations would apply to a gas forming a surface layer on a piece of metal or on a solid or liquid, and may account for the electrification observed when gases bubble through liquids.

In the case of salts in flames when there is also ionization, it is to be remarked that the ionization is not of the type that would be produced if the metal in the salt were positively electrified and the acid radicle negatively; for in this case the carriers of the negative electrification are corpuscles and not negatively electrified atoms. The charging up of the positive ion in the flame may be analogous to the emission of negative corpuscles from hot metals.

L. Bloch (*Annales de Chimie et de Physique*, xxii. pp. 370 & 441, xxiii. p. 28), who has made a very interesting series of experiments on the connexion between chemical charge and ionization, found that the flame of burning sulphur did not conduct when its temperature was below 400° C., but had great conductivity when the temperature was raised to a much higher value. He further showed that in the many cases of chemical action on which he made observation, which included the dissociation of arseniuretted hydrogen, the oxidation of nitrogen bioxide, the action of chlorine on arsenic, the chemical action was not accompanied by ionization.

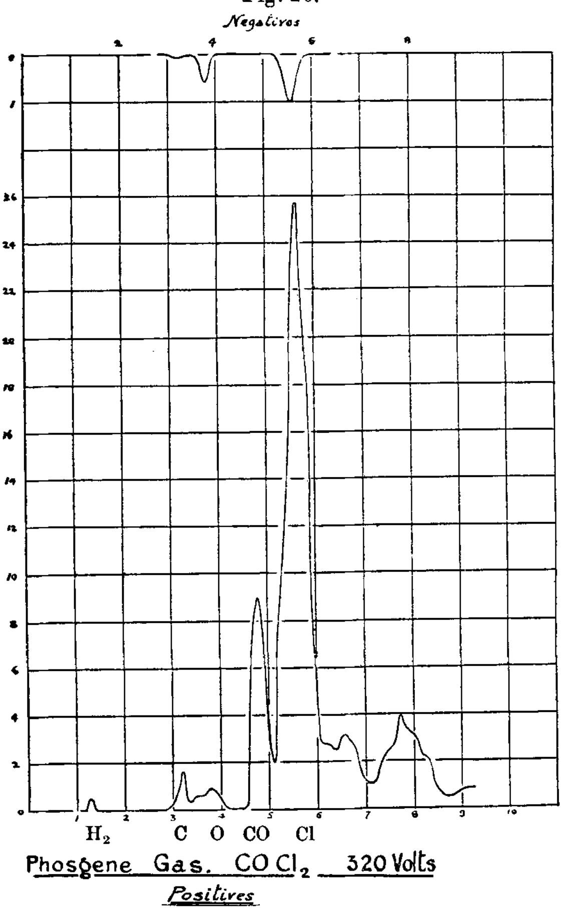
The Faraday cylinder method may be used to obtain information as to how the various atoms in a complicated molecule are linked together.

A curve got by the use of the Faraday cylinder method when the discharge passed through phosgene gas $COCl_2$, is shown in fig. 26. The curve shows that the carriers of the positive electricity were the atoms of C, O, Cl, the molecule of CO, Cl_2 and CCl and $COCl_2$; the negative carriers were C, O, Cl. It will be noticed that only a small fraction of the current is carried by free carbon and oxygen atoms, showing that in phosgene the carbon and oxygen atoms are so firmly united that the greater part of them remain combined even when the gas is dissociated. Fig. 27 is the curve for CO_2.

Retrograde Rays.

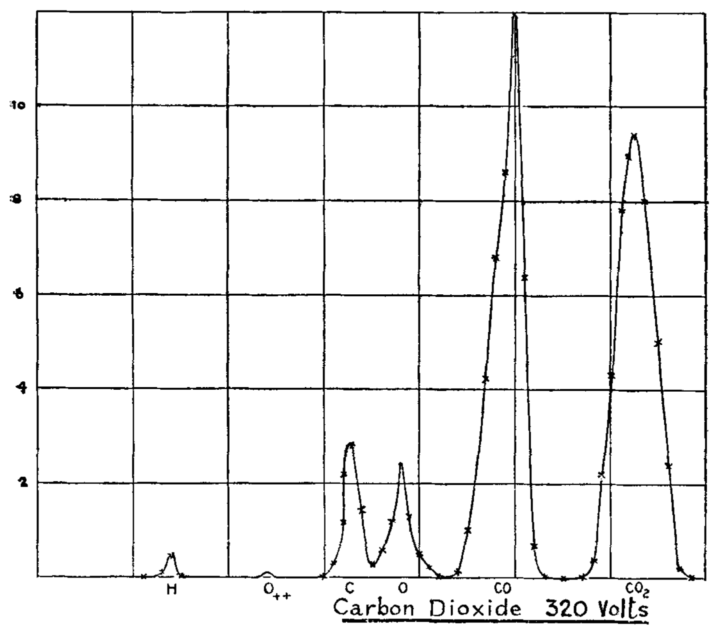
The existence of positively electrified particles moving away from the cathode was observed by Villard (*Comptes Rendus*, cix. p. 42) and the author. I have recently succeeded in obtaining a photograph of these rays. The method employed was to use the perforated electrode which in the previous experiments had served as the cathode for the anode, and to use for the cathode a flat plate of aluminium placed so that the normal to its plane passed through the hole in the other electrode. By giving an exposure of over an hour and using a larger tube (about 1 mm. in diameter) for the perforated electrode, I have

Fig. 26.



succeeded in getting photographs of these rays, one of which is reproduced in fig. 28 (Pl. IX.); the definition is not good owing to the size of the tube. But in the photograph can be seen rays corresponding to the hydrogen atom and molecule and to the oxygen atom. An interesting point about the photograph is that the negative side (the left) is stronger than the positive, and shows negatively electrified hydrogen atoms and molecules and oxygen atoms. Thus, in addition to the cathode rays and positively electrified retrograde rays, we have streaming from the cathode negatively electrified atoms and molecules; the photograph shows that the maximum velocity of the negative atom is about the same as that of the corresponding positive one. This, I think, confirms the view I expressed in a former paper that these positive retrograde rays are atoms or molecules which get negatively

Fig. 27.



electrified near the cathode, are then repelled from it by the electric field, and subsequently, by collision, lose a negative charge and acquire a positive one. The photographs show, since the negative side is stronger than the positive, that in this case the majority of the charged atoms had retained their negative charge.

I wish to record my indebtedness to Mr. F. W. Aston, B.A., whose skill in designing and making the numerous pieces of apparatus required in these investigations has been of the greatest assistance, and also to Mr. E. Everett.

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Fig. 2.

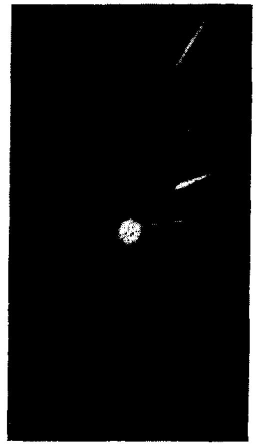

Fig. 3.

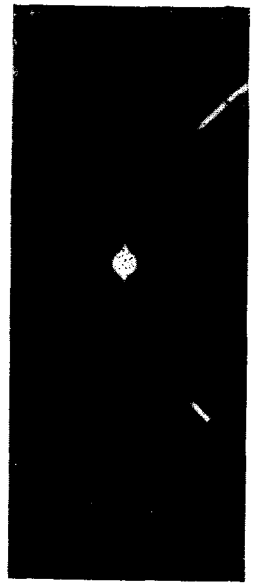

Fig. 4 *b*.

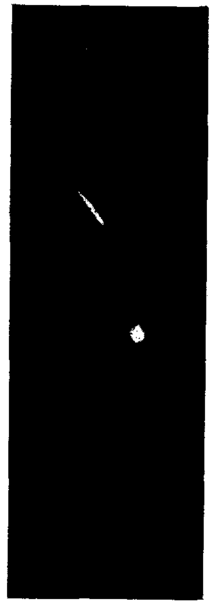

Fig. 5.

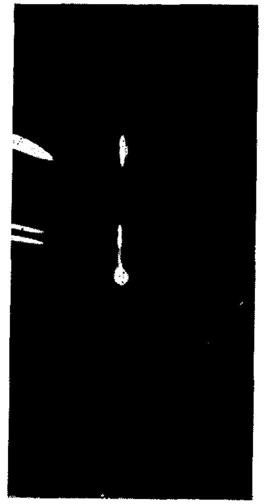

Fig. 8.

Fig. 9.

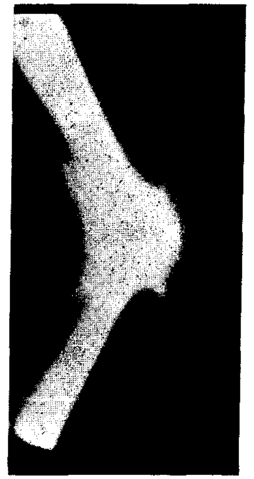

Fig. 11.

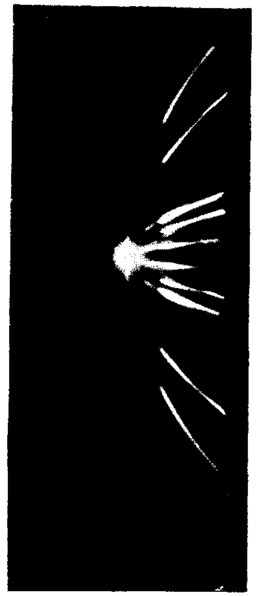

Fig. 12.

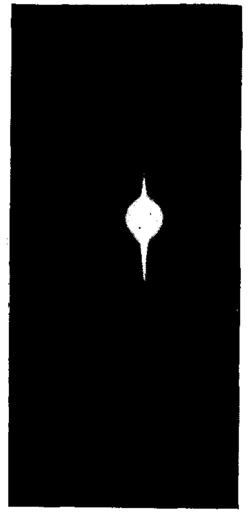

Fig. 13.

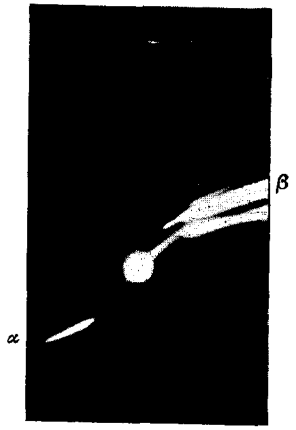

Fig. 14.

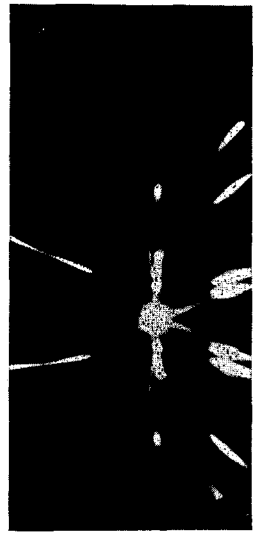

Fig. 15.

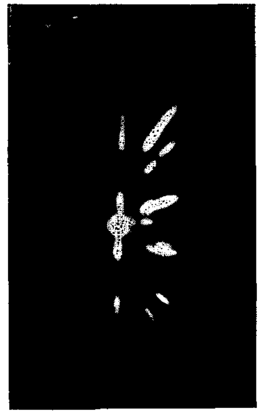

Fig. 16.

Fig. 16 *a*.

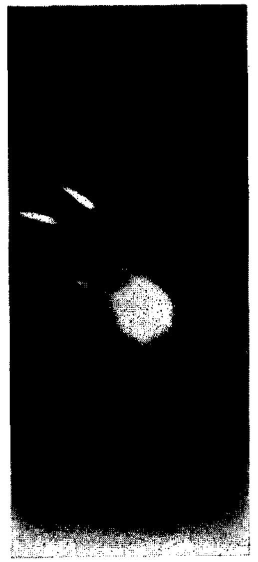

Fig. 17.

Fig. 18.

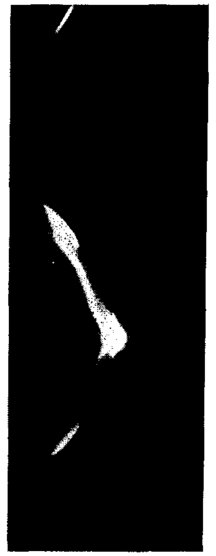

Fig. 20.

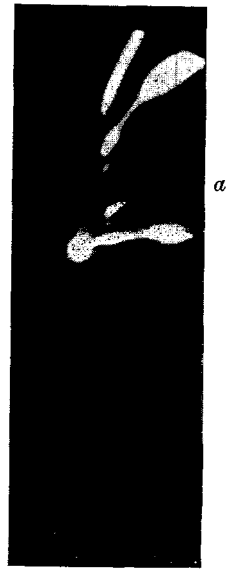

Fig. 21 *a*.

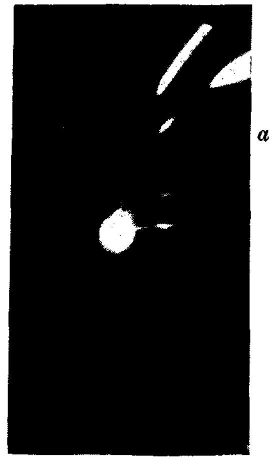

Fig. 21 *b*.

Fig. 21 *c*.

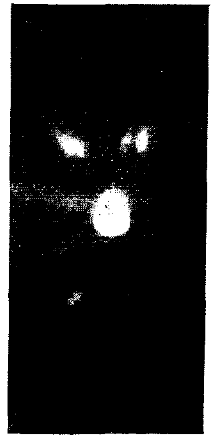

Fig. 28.