

THE BAKERIAN LECTURE. "Experiments on the Discharge of Electricity through Gases. Sketch of a Theory."* By ARTHUR SCHUSTER, Ph.D., F.R.S. Received May 7. Read June 19, 1884.

[PLATE 4.]

In the following pages I give an account of several new phenomena, some of which have a direct bearing on the theory of the discharge of electricity through gases. Although I hope that the experiments may be judged independently of any theory, their description may be rendered a little more clear and interesting if I begin with a short explanation of the theoretical views to which they seem to me to point.

These theoretical conclusions will be looked at favourably, I think, by those who have been trained up with the ideas of Faraday and Maxwell; for they must have always considered it likely that the conduction of electricity through gases is more probably due to something resembling the electrolytic conduction in liquids than to the direct passage of electricity from one molecule to another. My experiments with mercury vapour argue very strongly in favour of this view.

Fundamental Points of the Theory.

I know, from private conversations, that many of those well able to judge consider some electrolytic action in a gas as probable whenever an electric discharge takes place through it. But owing, no doubt, to the want of experimental evidence, very little has been published bearing on this point. Mr. J. J. Thomson† has recently supported this view. His ideas are of utility for the explanation of some phenomena attending the spark discharges, but they furnish no clue towards the explanation of the asymmetry of the glow discharge, and of some appearances which by many are considered as characteristic and fundamental in the passage of electricity through gases. No consistent attempt towards a systematic theoretical discussion of these facts has yet been made.

I am afraid that I can only offer a very crude beginning of such a discussion, but I have sufficient confidence in the correctness of its fundamental views to submit them to the judgment of the scientific

* I have not in this preliminary paper been able to do full justice to those to whose labours I think it is chiefly due that this subject has become ripe for theoretical deduction. I may mention here the names of De La Rue and Müller, Crookes, Goldstein, Gustav Wiedemann and Rühlmann, and Eilhard Wiedemann; but the two authors whom I have most often found it necessary to consult are undoubtedly Faraday and Hittorf.

† "Phil. Mag.," June, 1883.

public. I shall avoid as much as possible all suppositions and hypotheses which cannot be put to the test of experiment; but it seems necessary to start with some assumption, in order to avoid too great a vagueness in the subsequent explanations. The assumption which I shall make is this: In a gas, the passage of electricity from one molecule to another is always accompanied by an interchange of the atoms composing the molecule. I have been much struck with the results of some experiments recently made by Mr. L. J. Blake in Professor von Helmholtz's laboratory; investigating the vapours rising from the surfaces of warm liquids which were kept charged to a high potential, he found that these vapours were entirely unelectrified. Different liquids were tried—such as pure water, water containing salts in solution, and mercury. Now, if it is found, that the vapour actually rising from an electrified liquid is not electrified, can we imagine that a molecule striking an electrified surface in its rapid motion should carry away with it any part of the electricity, or that one molecule should be able to communicate electricity to another in an encounter? Assuming that we cannot, we are led at once to the supposition that the discharge in gases is accompanied by a breaking up of the molecules. But this does not seem to me to be quite sufficient to account for all phenomena, and especially not for those involving stratifications. There is reason to think that the formation of unstable compounds, such as ozone, plays an important part in the glow discharge. It is very likely essential to the production of stratifications.

The test of any theory must be found in the numerical results it is capable of giving. Hitherto, however, the qualitative phenomena have not, in my opinion, been sufficiently separated from the great number of disturbing effects to allow us to give a decisive value to quantitative measurements. Though I shall not discuss the few measurements which I have been able to make, I shall point out where numerical results can be most easily obtained by the theory and tested by experiment. I do not pretend to explain all the phenomena of the discharge, but I shall attempt to show that there is no distinct contradiction between the theory, in favour of which I argue, and the facts; that is more than can be said of any other theory that has been proposed. I shall try to prove in the present paper that the molecules are, in all probability, broken up at the negative pole.

Experiments with Mercury Vapour.

According to the kinetic theory of gases, the molecule of mercury vapour consists of a single atom, which is incapable of vibration. Mercury has a very brilliant spectrum, which proves that the theory is incomplete in some important point. It is well known, on the other hand, that the theoretical conclusion receives support from the

fact that the vapour-density of mercury vapour is anomalous. If, as is generally supposed, the molecule of the simple gases contains two atoms, that of mercury can only contain one. At any rate, we are justified in asserting that the molecule of mercury vapour has a simpler composition than that of most gases. If, then, an essential part of the glow discharge is due to the breaking up of the molecules, we might expect mercury vapour to present other and much simpler phenomena than the gases with which we are generally accustomed to work. *This, indeed, is the case; for I find that if the mercury vapour is sufficiently free from air, the discharge through it, shows no negative glow, no dark spaces, and no stratifications.* In view of the importance of the fact, I have paid a good deal of attention to this point, and, in spite of some experimental difficulties, I have considerable confidence that the statement which I have made is true. The one fact which up to recently has made me speak with caution consists in the altered conditions under which the experiments with mercury have to be carried on, but I think that I have now a complete answer to the objection which might be raised on that ground.

One difficulty consists in the choice of electrodes. Aluminium is attacked by mercury vapour, and experiments made with aluminium might therefore be objected to as not conclusive. Platinum is the only metal which can be conveniently used, but platinum blackens the tube very rapidly and prevents the examination of the parts surrounding the negative electrode. I have found it convenient to use platinum electrodes surrounded by a small glass tube open at its end. The discharge can then pass freely from the open end, and the glass tube prevents the deposit of platinum in the outer tube. But the platinum may even protrude to a small extent, as the deposit, unless it is thick, seems to combine and alloy easily with the mercury in the tube. If the glass tube surrounding the metal electrode does not fit too closely the discharge will partly pass through the interstice and heat up the glass, which then becomes a sufficiently good conductor to allow the discharge to pass through it, which is an advantage, as the electrodes then have a larger area of active surface. My tubes had two such electrodes, and contained also a quantity of mercury, varying perhaps from 1 to 4 cub. centims. They were attached to a Sprengel pump. Both sulphuric acid and phosphoric anhydride were used for drying purposes. After all the air was as much as possible exhausted, the mercury was heated up to its boiling point. When this had repeatedly been done and the tube kept at the pump for at least a day, the discharge from my coil, which gives a good 4-inch spark in air, would not pass, and there was not a trace of fluorescence. Aluminium electrodes gave more trouble than platinum ones, for they seemed to contain much more hydrogen.

It is needless to describe all the tubes used and the experiments

made. I have varied the conditions of the experiments in many ways, but always with the same result. When the air was sufficiently expelled, the spark does not break through the tube at the ordinary temperature; when the mercury is heated the discharge passes, but always in a perfectly continuous stream, joining the positive and negative electrode. It is difficult to prevent small bubbles of mercury from condensing on the surface of the glass, and the absence of dark space and glow might be explained by the irregularities thus introduced, but I think the following observations conclusive in this respect.

The mercury in the tube would always at first contain small bubbles of air between it and the glass, and these could be purposely left, say, on one side, by volatilising the mercury always on the other. One tube could in this way be prepared which, with a small but visible bubble on one side kept down by the mercury, did not allow the discharge to pass. If the mercury was heated without disturbing the bubble, the current passed, illuminating the tube with a perfectly continuous stream of light. As soon, however, as the bubble was driven into the tube, a perfectly distinct and clear dark space became visible at once.

The following observation was also repeatedly made. As the electrodes generally contain a large quantity of air dissolved in them, I have been accustomed to send through my various tubes a very strong discharge, using a Wilde dynamo machine as a primary current. The currents thus obtained I have found very useful in driving out the air from the electrodes. While the mercury was kept hot a strong current was thus sent through the tubes. Instantaneously a dark space appeared surrounding the negative electrode; the appearance presented was that of a discharge through mercury superposed on one through air, and whether these discharges passed through the tube simultaneously or one after the other, the result proved that the dark space and glow can and generally do appear under the exact conditions under which they are absent in mercury vapour. The strong current of the dynamo machine has generally been fatal to the life of the tube, and I am not sure that I have ever been able to examine the discharge from electrodes really free of air. To that small remnant of air it is due, perhaps, that the discharge, though continuous, was seldom quite symmetrical with respect to the two poles. There generally seemed to be a tendency to surround the negative, and to set out only from the point of the positive electrode. But the appearance was much disturbed by globules of condensed mercury on the electrodes; sometimes both electrodes were equally surrounded by the discharge, and sometimes the latter would pass only from the points.

[There are, however, other causes at work which tend to produce

an asymmetry. I have noticed a very curious tendency of the discharge at the negative pole, to start rather from the glass out of which the electrode protrudes, than from the metal electrode. The glass is heated up in that case and a bright yellow, sodium spot is seen at the point from which the current in the vapour sets out. When the discharge sets out from the metal an amalgam of mercury and platinum, or mercury and aluminium, is formed. The subject requires further investigation.—July, 1884.]

It is more difficult to prevent stratifications than to prevent the dark space and glow. A mixture of air and mercury shows beautiful stratifications. When the air is expelled as much as possible, I never saw stratifications while the tubes were attached to the pump, but in order to study the phenomena a little better I sealed off some of the tubes and heated them up either in a steam or paraffin bath, so as to give them the same temperature throughout. It is then that the stratifications are very apt to occur at a temperature of 100° C., when the tension of mercury vapour would, according to Regnault, be three-quarters of a millimetre. The extreme difficulty, however, of excluding all traces of air easily explains this, while the irregularity of the phenomenon, and its absence in the experiments which were carried on with the greatest care, seem to me to be conclusive in proving that pure mercury vapour never shows any stratifications, for the experiments were continued until the tension of mercury vapour was 20 millims.

My assistant, Mr. Arthur Stanton, has taken some photographs of the spark in mercury vapour at different pressures.

Figs. (1*a*) and (1*b*), Plate 4, represent the spark in mercury at a uniform temperature of 50° . The tension of mercury vapour at that temperature according to Regnault is 0.1 millim. Figs. 2*a* and 2*b* represent the discharge at a temperature of 100° and a tension of 0.7, while in figs. 3*a* and 3*b* the temperature was 150° and the tension 4.3 millim. In the figures marked *a* the pole on the left hand side was negative, while in the figures marked *b* the negative pole was to the right. The electrodes were platinum wires surrounded by glass tubes open at the end; and in figs. 2 and 3 the tendency of the discharge at the negative pole to start as far back as possible from the glass, rather than from the metal, is well seen.

I have reason to think that the vapour of sodium resembles that of mercury, and does not show any dark intervals. From the fact that at the temperature of the spark sodium shows its line spectrum instead of the bands, we may conclude that we have also to deal in that case with a monatomic molecule.

Evidence of Dissociation during the Discharge.

There is very strong spectroscopic evidence that gases through

which an electric current is passing are always in a state of rapid dissociation. Thus I do not know of a single case in which the gas during the glow discharge does not show two, or generally even three, distinct spectra in the same or in different parts of the tube. This dissociation seems especially strong in the negative glow. The characteristic spectrum which gases, as a rule, show in the neighbourhood of the negative electrode bears evidence of belonging to a complex molecule, but at the same time a high temperature line spectrum is always seen to overlap the bands. I have shown some time ago that the spectrum of the negative pole cannot be explained by mere peculiarities of temperature, and, further, that it must be due to the formation of a distinct molecule, as the spectrum keeps its original place even a short time after the current has been reversed.

As the subject is one that is not much studied, I may be permitted to give here a short account of the spectral phenomena seen in tubes filled with different gases.

Nitrogen.—This gas shows in the positive half a well-known complicated band spectrum. The glow shows peculiar bands, but the strongest nitrogen *lines* are also always visible, and it is generally only there that the lines are seen. The capillary part will only show lines when its bore is very small, as, for instance, when a piece of thermometer tubing is used. As the bands of the positive half are also seen in the glow, this region shows the superposition of three distinct spectra. There is at present no longer any doubt that this means the superposition of three distinct sets of molecules.

Oxygen shows phenomena exactly corresponding to those in nitrogen. The positive part as regards character shows what I have called the complex line spectrum, which stands in a remarkable way between a line and a band spectrum. The negative glow shows characteristic bands, and at the same time both the spectrum of the positive pole and traces of the high temperature line spectrum of oxygen. Here, again, we have three distinct sorts of molecules in the glow.

The phenomena in *hydrogen* are not as yet so well ascertained. The positive half and also the glow show generally a band spectrum which now is generally ascribed to hydrogen; but, at the same time, the lines are very strong. I do not know whether a peculiar spectrum has ever been noticed or looked for at the negative pole, but, owing to the complexity of the band spectrum, it would be rather difficult to discover. No gas shows greater difficulties of purification, and therefore the spectroscopic appearances are much more doubtful in this than in the other gases.

Carbon compounds show their characteristic spectra whenever they are not very rapidly decomposed; but at the same time they always show at least in the negative glow the true carbon spectrum. I have

already on a former occasion drawn attention to the very suggestive fact that the compounds in which the molecules are made up of two or more carbon atoms (cyanogen, hydrocarbons) give the carbon bands, while those containing only one atom (carbonic oxide) show the true line spectrum of carbon. Ångström and Thalén observe that the violet line of carbon is generally visible in tubes filled with carbonic oxide, but I have only observed this line in the negative glow, where it undoubtedly is visible even when no trace of it can be seen in any other part of the tube. I have also observed that tubes filled with carbonic oxide show a band peculiar to the negative pole. Though this observation is nearly ten years old, I have hitherto left it unpublished together with other matter bearing on the same point, as I had hoped to find time to complete my investigations and to write a general description of the spectra of carbon compounds.

I do not think that any of the other gases have been sufficiently well investigated to be noticed here; but some observations which I have made at different times on the spectrum of chlorine confirm the general conclusion which I have drawn.

Messrs. De La Rue and Müller have noticed in some of their experiments a sudden expansion of the gas when the discharge was sent through it. They have proved that this expansion is not due to increased temperature, and a breaking up of the molecules into atoms seems to me to be its next natural explanation.

While we thus have ample evidence of dissociation whenever an electric current passes through a gas, we also find that whatever increases independently the dissociation improves the conducting power of the gas. Thus we know that a flame is a good conductor, and Hittorf has, in a series of very interesting experiments, shown that if we heat up the electrodes to a white heat, an electromotive force of a few volts will send a current through the gas.

The fact also discovered by Hittorf, that if a discharge is set up a small electromotive force is sufficient to pass a current across, is also easily explained by our theory, as the original discharge throws the molecules into that state of dissociation which favours the passage of the current.

On the Influence of a Positive Electrode on the Negative Glow.

I now pass to the description of a series of experiments which seem to me to be only capable of explanation by the views brought forward in this paper, and I should like therefore to consider them as crucial experiments which have to be explained by any true theory of the electric discharge.

It was up to recently believed that the form and extent of the negative glow was determined only by the shape of the negative electrode, but was independent of the shape of the vessel or the

neighbourhood of another electrode. Goldstein has, however, described some effects of negative electrodes on each other, and E. Wiedemann has recently made an experiment in which some remarkable effects were seen on the approach of the positive electrode to the kathode. Professor Wiedemann's experiment belongs to the same class as those presently to be described, but differs from mine in so far as it refers to very great exhaustion at which the glow is no longer visible, while I have generally worked at much higher pressures and especially studied the effect on the glow. The peculiarity of the arrangement which I have used consists in the large size of the negative electrode, which allows a much easier observation of the parts at which the negative glow chiefly settles. I shall show that it tends to accumulate *away* from the positive electrode.

The glow which surrounds the negative electrode is divided into three layers which are, however, only clearly separated when the pressure has been reduced to the fraction of a millimeter. The first layer narrow, and closely surrounding the negative electrode, is with new electrodes of a beautiful golden colour. Its spectrum is chiefly made up of the hydrogen and sodium lines. The sodium is evidently due to matter which has settled on the metal, and the hydrogen comes out of the metal where it was absorbed. In time these lines disappear, the layer loses its golden colour, and the spectrum is now that of the positive half of the discharge. The second layer is the so-called dark space. The name is a good one, although Goldstein has pointed out that this layer is only relatively not absolutely dark. Its luminosity depends much on the gas used. With nitrogen it seems to me to be much darker than with the hydrocarbons. The thickness of this dark space is according to the measurements of Puluj about forty or fifty times as great as the mean free path in air at the same pressure. But the thickness depends on many circumstances, and would not, according to Puluj, be quite proportional to the mean free path at different pressures as we should expect it to be; but measurements of this sort can be only very approximate at present.

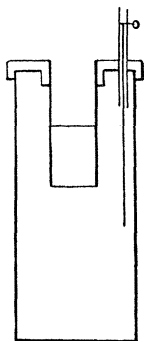
The third layer is the glow proper. When the curvature of the electrode is small its inner boundary is sometimes defined with quite a remarkable sharpness, but this also depends on the gas which is used. The outer boundary of the glow extends to different distances, according to the intensity of the current, the size of the electrode, and partly also its shape. It would be useless at present to enter further into the different causes which influence the thickness and definition of these different layers.

The glow is separated from the positive part of the discharge by a non-luminous space, sometimes also called the dark space. In order to prevent confusion I propose the name "dark interval" for it.

I have used in my experiments on the glow a cylinder open at one

end. Its internal diameter was 15 centims., its height 38 centims. The open end was closed by means of a brass disk into which a groove had been cut. The rim of the open end of the cylinder was cemented into this groove. A circular hole 5.5 centims. in diameter was cut into the centre of the brass disk, and another glass cylinder was fitted into this hole. The negative electrode was formed by a piece of aluminium foil 8 centims. long, which was wrapped round the inner cylinder. The electrode had a surface therefore of over 120 square centims. A long aluminium wire running parallel to the axis of the aluminium cylinder at a distance of about an inch formed the positive electrode. The aluminium cylinder was connected metallically to the brass disk, so that the positive electrode had to be insulated from it. This was done by passing it through a glass tube which was cemented into the brass plate. This tube also formed the opening through which the exhaustion could be carried on. The aluminium wire had, of course, to be connected with a platinum wire sealed into the tube. The accompanying figure shows a section of the vessel.

Fig. 1.



As an air-pump I have used Hagen's form of the Toepler mercury pump. As the vessel to be exhausted was rather large, the exhaustion was a little laborious, and had to be carried on with great care. I need hardly add that the effects to be described are not the result of a single experiment, but that the vessel was often refilled and exhausted in the course of them. I shall now describe what is observed on exhaustion.

At first the discharge, of course, only passes as a spark. It runs irregularly along the wire and passes to the nearest point of the aluminium cylinder. Gradually the glow settles down on the cylinder, if that is negative, as I shall assume it to be. The glow is quite irregular and not always at the same place, but a tendency to avoid the place opposite the wire is already apparent. In fact the effect

was first discovered at this stage of the exhaustion. The glow gradually becomes wider. At first it confines itself to the half-cylinder which lies towards the positive wire, but it is very irregular in shape. During the first exhaustion, it was interesting to notice how on one day there were some spots on the aluminium cylinder which were illuminated with especial brilliancy by the glow, while on the next the same spots were remarkable by the absence of any glow above them. All these effects depend of course on the state of the aluminium surface; gradually this becomes more uniform and the glow more steady.

On exhaustion the glow gradually covers the whole aluminium surface; but a dark strip about 2 or 3 centims. in width is observed directly opposite the positive wire. The appearance is well represented by fig. 4, Plate 4, representing a photograph taken of the phenomenon. I shall refer to the dark strip as the "dark area." As exhaustion proceeds, the glow extends further into the vessel. The dark space surrounding the cylinder becomes more apparent and expands, but the dark area loses its sharpness. Fig. 5 represents a photograph taken at this stage. The dark area increases slightly in width with decreasing strength of current.

When the cylinder is positive and the wire negative, very little is seen of the positive part of the discharge. At pressures of about a millimeter two reddish-yellow bands are noticed running parallel to the axis of the cylinder on either side, and symmetrical to the wire. They are too faint to be photographed. When the exhaustion is carried further these bands become less and less distinct, and gradually disappear.

I shall describe in another part of the paper some curious phenomena which are seen on sudden reversal of the current either in one direction or another, also the effects of a magnet inside the aluminium cylinder on the glow surrounding it.

Explanation of the Repulsive Effect of the Positive Electrode on Glow.

The following seems to me a plausible explanation of the phenomenon which I have just described. The rapid fall of potential which is observed on crossing the negative electrode suggests at once, independently of any theory, that we have to deal with the action of a condenser, for we know that no statical charge can produce a finite difference of potential at the electrode, while a double layer will produce a discontinuity. Although it may not be proved that an absolute discontinuity of potential exists at the kathode, it is yet certain that a very rapid fall takes place. This is all that is necessary for the argument.

We recognise such a double layer in the case of electrolytes, but

there is an essential difference in the thickness of the layer within which we must imagine that condenser action to take place. In the liquids that thickness must be very small, as is shown by the intensity of the observed polarisation currents. The positively electrified matter in every case is kept against the negative surface by a joint action of electrical and chemical forces, for it has been shown by Helmholtz that only thus can we explain a difference of potential between two bodies. It is the chemical forces which keep the two electricities asunder. The gaseous molecules or atoms, however, subject to their mutual encounters, and always having certain velocities, will tend to leave the surface. They are kept near the surface by the electrical forces. I do not, of course, mean to imply that the positive part of the condenser is always made up of the same molecules, but only that the time during which each positively electrified particle forms part of the condenser is large compared to the time during which it would be in the neighbourhood of the electrode if they were both unelectrified.

Suppose, now, that a positive electrode is placed near such a condenser. The resistance of the gas is so much greater than that of the metal electrode that we shall assume the whole electrode to be of the same potential. The lines of force will then cut the surface at right angles, and could we assume the condenser to be infinitely thin, there would only be a normal force acting on its particles; but as the lines of force are curved, the particles not in immediate contact with the surface are acted on by a tangential force which will tend to drive them away from the positive electrode. As a steady state will only be possible when the total force is normal throughout the condenser, we arrive at the condition for the steady state that within the condenser the fall of potential must be the same for equal distances measured along the normal to the surface.

Some idea of the distribution of potential may be gained by considering a positively charged point near two concentric spheres, the inner one of which is charged with negative electricity. The outer sphere representing the outer coating of the condenser will act as screen; the distribution on the inner sphere will therefore be uniform. The analogy is, of course, not complete, as we cannot assume the positively electrified particles to be distributed over a surface merely.

Our experimental evidence speaks in favour of the conclusion to which we have arrived, namely, that the fall of potential is equal for equal distances taken normally away from the negative electrode. This seems to follow at least from the fact that the boundary of the dark space is, whenever that is possible, equidistant from the electrode, for we know that the width of the dark space depends on the intensity of current. When the electrode is of such a shape that the normal drawn outwards from it meets its surface again, or whenever

negative electrodes are near one another, more complicated phenomena arise which we need not discuss here.

It is curious to observe the boundary of the dark space when the electrode is a cylinder. Round the surface of the cylinder the boundary of the dark space is a concentric cylinder. Opposite the end of the cylinder it is a plane, and the plane and cylinder are united by means of a surface, which is the envelope of spheres drawn with the same radius from the circular edge of the cylinder as centre, that is to say, by means of a part of a circular ring made up of quadrants. Goldstein has described similar forms of dark spaces. The point of interest, however, is this: that while on the cylindrical and plane surfaces the boundary of the dark space is well marked and bright, it is extremely indistinct on the circular ring. The amount of electricity crossing each part of the surface seems to be the same, while wherever the lines of flow separate the intensity of the current must decrease. We obtain in this way a smaller intensity of current at the annular surface.

Hitherto we have only assumed a certain number of particles positively electrified in the immediate neighbourhood of the negative electrode, and we have left it altogether undecided what these particles are. But if we consider now the fact that the glow does not appear opposite the positive electrode, that is to say, that while the fall of potential is the same all over the surface, the flow is stronger at some places than at others, we are driven to the conclusion that the flow does not altogether depend on the fall of potential, and we must again look for an explanation in the chemical as well as the electric forces. Wherever the fall of potential is chiefly produced by the presence of the positively electrified particles, which I now assume to be the decomposed molecules of the gas, these will help by their chemical action to decompose other molecules. Opposite the positive pole the fall of potential is principally due to nearness of that electrode; chemical forces are absent, and the molecules will not be decomposed. This is, I believe, the explanation of the dark area. And it brings with it the explanation of a large quantity of other facts, as, for instance, the one which has been so long observed and well established, that once a current is set up in the gas it requires a much smaller electromotive force to keep it going. For the discharge, according to us, will generally be introduced by a spark which must give the first supply of decomposed molecules before the continuous glow discharge can establish itself.

The effect of an increase of current on the dark area is also easily explained, but I do not propose to go into details in the present paper.

If my explanation is true, we must expect the glow to be strong between two negative electrodes, and that is the case.

I may for the sake of clearness once more mention shortly the principal points of the argument.

The rapid fall of potential in the neighbourhood of the negative electrode renders the presence of positively electrified particles in its neighbourhood necessary.

If the distance through which the condenser action takes place is sensible, the positively electrified particles will be acted upon by a neighbouring positive electrode.

A steady state will be established in which the fall of potential along the normal from the surface will be everywhere the same.

As however the flow is stronger away from the positive electrode, we must conclude that other forces besides electrical forces determine the flow.

It is natural to assume that these are chemical forces: that in other words the positively electrified particles are the decomposed molecules, which by their presence assist the decomposition of others, and therefore the formation of the current.

Unless a flaw is detected in this line of argument, I think that the conclusion must be granted, namely, that the decomposition of the molecules at the negative electrode is essential to the formation of the glow discharge. This is really all that I endeavour to support in this paper. The rest can only be settled by further experiments. And amongst the rest I count also the primary cause which originally produces the decomposition of molecules at one pole rather than at another. It is possibly due to an electromotive force of contact between the gas and the electrodes which tends to make the gas electronegative.

It does not seem difficult to explain by our theory the phenomena which happen at the negative electrode on exhaustion. When the pressure is high the discharge passes in a series of distinct sparks, separated by a sufficiently long interval of time to make each spark independent of the one preceding it. Here, of course, the spark will set out from that part of the negative electrode at which the tension is strongest. As the vessel is gradually exhausted the sparks succeed each other more rapidly, and the molecules decomposed during one discharge assist the next discharge. If the decomposition of the molecules goes on at a sufficiently rapid rate the tangential action of which I have spoken comes into play, and the negative glow will cover a greater part of the negative electrode. The discharge at the same time can become continuous, for the state of polarisation near the electrode can keep up a continuous stress. The stronger the current becomes, the more easily will the negative electrode become covered with the glow.

The Dark Space and Glow.

I enter now into a more detailed account of the phenomena which happen in the neighbourhood of the negative electrode. We consider this electrode to be surrounded by a layer of electro-positive particles. The molecules are decomposed partly by chemical and partly by electrical forces, and the electro-negative part will be able to follow the forces acting on it, and acquire a considerable velocity within a small distance. This velocity will gradually be reduced by impacts, and the temperature thereby raised: hence the luminosity of the glow. The dark space must, therefore, be considered as the region through which the greater number of atoms can freely pass. But, as already observed, the dark space is itself slightly luminous, as it should be. We cannot, of course, know anything at present as to the mean free path of the constituents of the decomposed molecules, especially as they move in a non-homogeneous atmosphere, traversed from one side by the molecules coming from the positive pole, and from the other by the products of decomposition. The chief difficulty seems to me to be the explanation of the sharpness of the boundary of the dark space in certain cases.

Mr. Goldstein has described some interesting experiments under the title of "A New Kind of Electrical Repulsion." I think that his experiments admit of a very simple explanation. When the glow is allowed to fall on a screen through which a small aperture is cut, its rays are seen to be propagated in straight lines from the aperture. If such a ray passes close to another negative electrode it is deflected. This seems to me to be a necessary consequence of the fact that the potential in the neighbourhood of an electrode alters very rapidly, and that therefore strong forces must act on a passing particle charged with negative electricity. Mr. Goldstein finds that as long as the two kathodes are metallically connected the effect is the same, whatever the pressure of the gas, whatever the nature of the gas, and whatever the strength of the current. All these laws are easily deduced from our theory. The velocity is acquired in the immediate neighbourhood of the negative electrode; if the fall of potential is increased in a given ratio the square of the velocity is increased in the same ratio, and throughout the path all the forces are increased also in the same ratio. Hence the path must be the same, and as neither the amount of electricity carried by each particle nor its mass would affect the result, the total deflection of the ray is independent of the nature of the gas.

Goldstein claims to prove that the repulsion is not exerted through solid substances like glass or mica, but his experiment admits of a better explanation. According to Hittorf we must consider the glow to be a good conductor, that is to say, metal wires which are placed

inside the glow readily take up the potential of the surrounding space. A screen of glass, therefore, in front of an electrode will become covered with electricity until the potential in its neighbourhood does not vary in a normal direction, and if the ray from a negative electrode passes tangentially, there can be no deflective force on the particles which make up the ray, the piece of glass will act as an electrical screen. We shall never be able to show for the same reason any deflecting force due to a statically charged body, for if the body is simply placed inside the vacuum, near enough to influence the current, it will discharge itself, and if it is covered with some non-conductor, that non-conductor will become charged on its outside until its effect on the lines of force has been counterbalanced.

A serious objection against Mr. Crookes' view that particles are projected from the negative electrode with great velocity has been first urged by Mr. E. Wiedemann, I believe, and was afterwards repeated by Goldstein. It would apply with equal force against the theory which I am defending. Particles moving with great velocity in one direction should send out light, the wave-length of which is affected by the motion. No such effect can be observed, although Goldstein has undoubtedly proved that the velocity must be sufficiently large to make it perceptible. But the particles moving with great velocity are not themselves luminous, that is proved by the existence of the dark space. It is only when their velocity has become sufficiently reduced and the energy is distributed in all directions, that the particles are luminous; but then we do not get a one-sided displacement, but only a very small widening due to the motion of the particles in all directions.

Mr. Crookes has given reasons why we should consider the region of the dark space as one in which directed motion prevails, and although Hittorf has raised serious objections against the arguments drawn from his radiometer experiments, which seem to be explained by secondary temperature effects, the general conclusion which he has drawn from his experiments is not thereby invalidated, for the rise of temperature itself requires explanation.

Proposed Test of the Theory.

The most conclusive proof of our theory would be the demonstration of the fact that each particle of matter carries with it the same amount of electricity. We shall not, of course, be able to prove this for each single particle, but I propose to show how we can decide the point experimentally as far as the average amount is concerned. Suppose a small straight beam is cut out of the glow and placed in a field of uniform force, the lines of which cut the rays of the glow at right angles. The force being everywhere normal to the rays, these will curl up in a circle. This has been shown to be true experimentally

by Hittorf. I think a careful measurement of the radii of such circles will give us important information, and I have already made preliminary experiments which have shown me that such a measurement is possible.

The force exerted on each part of the current is proportional to $v \times e$, where v is the velocity of each particle, and e the amount of electricity it carries. If the particle moves in a circle the force is also proportional to $\frac{v^2}{r}$ where r is the radius of the circle. Hence r must be proportional to v/e .

Suppose, now, that the current is increased. This may mean either that the number of particles carrying the discharge is increased, or that the velocity of each particle is increased, or that the amount of electricity is increased, or, finally, some combined effect of these three causes. When we come to consider the positive part of the discharge, I shall show that the number of particles taking part in the discharge seems certainly increased by an increasing current, and this is also evident from the mere appearance of the discharge; this does not, however, affect the influence of the magnet. I find as a result of experiment that the diameter of the rings is considerably increased by an increase in strength of the current; hence an increased current must either mean a larger velocity only, or, at any rate, a velocity increasing in a quicker ratio than the amount of electricity carried. Before going further we must consider in what way v depends on e . Let the total fall of potential in the region in which the velocity is acquired be F , then v will vary as the square root of Fe , and hence the diameter of the ring will vary as $\sqrt{\frac{F}{e}}$. If e is constant the diameter of the ring ought to vary as the square root of the fall of potential in the neighbourhood of the negative electrode. Here, then, we have a definite experimental problem before us which I hope to decide one way or another as soon as I have the necessary experimental means at my disposal. At present I wish only to point out that if e does vary there is every reason that it cannot vary otherwise on the average than proportionally to F . Hence the diameter of the ring ought to be independent of the current, which it is not.

Experiments with Hittorf's Tube.

Mr. Hittorf has described some phenomena which are, in my opinion, particularly interesting, as putting beyond all reasonable doubt the projection of particles away from the negative pole.

The tube, or rather the bulb, which he used had two parallel electrodes at a distance of only a few millimetres. It was found that at very low pressures the discharge from the positive electrode took

place not towards the negative pole, but in the opposite direction. I have repeated these experiments with electrodes which were rather further apart. The behaviour of the tube under different circumstances can be shortly expressed by saying that the discharge always passes to the nearest point of the inner boundary of the dark space. When the exhaustion is not sufficient, so that the width of the dark space is less than the distance between the electrodes, the positive discharge takes place towards the negative pole as in the ordinary tubes, but as the dark space gradually expands, the positive discharge contracts, and becomes invisible when the dark space comes into contact with the positive wire. On further reduction of pressure the dark space reaches beyond the positive pole, and the discharge passes from that pole to the nearest point of the negative glow. In other words, the tube behaves as if the glow, and not the negative wire, formed the electrode. But this is exactly what should happen according to our theory.

The negative particles which are projected from the wire have first to be brought to rest by molecular encounters before their motion is regulated by the electrical forces in the ordinary sense.

The experiment is conclusive to my mind, because in the neighbourhood of the positive discharge, as it turns away from the negative pole, we have the current flowing in two opposite directions at closely adjoining places. This could not be possible unless the current in one direction was carried by particles moving against the lines of force by their inertia. The positive discharge at the lowest pressures which I am able to obtain shows some curious phenomena, indicating perhaps that to some extent the phenomena of the negative pole are repeated to a much smaller degree at the positive pole. A dark line is noticed parallel to the positive wire at a distance varying with the pressure, and at the best exhaustion which I could obtain about 1 millim. distant from it. From the wire to the dark line the discharge is very narrow, but from the dark line it spreads out fan-like towards the negative glow.

Fig. 6, Plate I, is taken from a photograph, and shows the phenomena which I have just described. As far as the negative glow in these tubes is concerned, the repulsive forces from the positive pole make themselves very perceptible, so that the glow becomes stronger away from the positive wire, and the tube presents the curious appearance of two discharges from the two poles tending away from each other and towards the glass vessel. The current completes itself on the side of the vessel. This is clearly shown in a photograph (fig. 7), which represents a projection in a plane at right angles to the wire poles. These poles appear therefore as points, and the two discharges passing away from each other and joining over the glass are clearly distinguished.

Effects observed on Reversal of the Current.

I now pass to a short description of some curious effects observed on sudden reversal of the current. In my large vessels in which the dark area opposite the positive wire appeared, the phenomena seen when the wire was negative and the cylinder positive present little that needs mentioning in detail. The only trace of positive light is confined to two yellowish lines running parallel and symmetrical to the wire. We have here very likely to deal with the reaction to the repulsive effect on the glow. If, when these yellow bands are seen, the current be slightly interrupted for a short time and passed again in the same direction, these bands will appear perfectly steady from the beginning of the passage. If, however, before making contact in the same direction, a single spark be passed in the reverse direction, the two bands will at first appear close together and right opposite the negative wire, then quickly to move outward and to take up their final position. If, after the cylinder has been positive, the current is interrupted for a longer period of time, say five minutes, then the same effects as on reversal will appear. Thus it seems that a certain state has been established which dies away in something like five minutes, but which can also be made to disappear by a single spark in the opposite direction.

Similar effects, though not so striking, are observed with the wire negative. The dark area seems to take time to establish itself. A short interruption of the current will make it reappear fully from the beginning, but if either five minutes are allowed to lapse, or a spark in the opposite direction is passed through the vessel, the dark area will not be well developed to begin with, but is filled with a faint glow which, however, dies away rapidly. These phenomena are, I think, fully in accordance with the theory here suggested, for it is clear that the condenser action will take time to establish itself and to die away, just as in a liquid. The effects observed when the cylinder is positive are not, in my opinion, produced by such a condenser action at the positive pole, but are secondary effects depending on the changes in the glow. When the current is finally established, the glow will be strongest away from the cylinder, and the positive discharge will consequently set out from parts of the cylinder not directly opposite the negative electrode. Hittorf has already noticed that when the negative electrode consisted of a long wire, the glow was found on first making contact to start from the point and to run backwards, covering gradually the whole of the wire. This is perhaps the place to dispose of an objection which might be raised against the theory. There are apparently no appreciable polarisation currents like those observed in liquids, but I do not think that this is a very serious difficulty. We usually represent

the action which takes place at the poles in an electrolyte as a condenser action, and we can calculate from the measured capacity of the condenser the distance between the two charges of electricity. In the case of liquids, this distance is extremely small, and is given by Helmholtz in his Faraday lecture as the ten-millionth part of a millimetre. Though the total fall of potential in a gas which is measured by the moment of the condenser might be the same as, or even much stronger than in the liquid, the charges might easily escape detection, if the distance between the layers is say ten thousand times larger in the gas than in the liquid. The phenomenon of the dark area tends to argue in favour of a greater thickness of the region between which the condenser action takes place.

The Positive Part of the Discharge.

I cannot enter in the present paper fully into the phenomena which happen in the positive part of the discharge. It is too early as yet, I think, to form a distinct idea as to how the electricity is conveyed in the manifold forms which the discharge seems able to take. But a few remarks may not be out of place to show that we meet with nothing that is contradictory to the theory which I have put forward. A remarkable result obtained in different ways by Hittorf and by E. Wiedemann is on the contrary rather in its favour. Hittorf has found that the fall of potential in that part of the tube which we have for convenience' sake called the positive half, is independent of the intensity of the current passing through it. This means that the current into the resistance is a constant quantity for a given tube and pressure, or in other words, that the energy dissipated is directly proportional to the current, and not to the square of the current as in a metallic conductor. It had, indeed, been found previously by E. Wiedemann that the heat developed in a series of discharges is proportional to the quantity of electricity which has passed through the tube, and independent of the fact whether that quantity has passed in a few strong sparks or in a greater number of weaker ones. This fact seems to point to the conclusion that in the positive part of the discharge a greater intensity of current only means that a greater number of particles takes part in the discharge, but that the velocity of diffusion of the particles carrying the discharge is independent of the intensity of the current.

With regard to the stratifications, I should offer the following preliminary explanation, but only with the view of showing that the theory is capable of dealing with these phenomena. In the first place stratifications are seen at their best with compound gases, and also with mixtures of gases which are likely to form compounds. That the decomposed particles at the negative pole are liable to form

compounds is shown by the peculiar spectrum of the glow in many gases. Such a compound will behave as an electrified molecule, and travel towards the positive pole, the fall of potential will increase its velocity, and that will again be reduced by molecular encounter, the heat thus generated will possibly decompose the molecule again; we have then two ways in which the discharge can be carried, either by the electrified molecules or by the decomposed atoms. If, owing to some reason, the decomposing of molecules takes place at definite places in the tube instead of being distributed unequally throughout the tube, we have what practically becomes a secondary negative pole with its dark space. There is much to be said in favour of the view that the intervals between two stratifications are due to the same causes which produce the dark space at the negative electrode. It is needless at present to speculate on the original cause which fixes the positions of these secondary poles.

I can see nothing antagonistic to our views in the secondary negative poles discovered by Goldstein to exist wherever the width of the tube rapidly widens in the direction from the negative to the positive electrode.

The Influence of the Magnet on the Electric Discharge.

The influence of the magnet on the electric discharge is generally supposed to be well understood, but a good deal yet remains to be said on the matter, for although we can in each individual case trace out pretty well why a certain effect happens, it is yet impossible, according to the results given hitherto, to predict beforehand the behaviour of a vacuum tube in the magnetic field.

The magnetic influence on the positive part of the discharge is either compared to the effect on an elastic thread carrying a current, or looked on as an effect on particles projected with great velocities from the positive pole. I do not think that either of these views gives a correct representation of the matter.

Let us compare for a moment the effects which are observed when a magnet acts on currents passing through liquids and gases. Supposing a liquid cell is placed equatorially in a magnetic field, strong movements of the liquid are observed, yet the lines of flow of electricity seem to be unchanged. I consider that the first effect of the magnet on a current through a gas is exactly the same; but then comes the difference. The particles of the gas which have carried the discharge conduct better than those which have not, and consequently the spark continues to pass through the particles which have been thrown aside by the magnet; that is to say, the current becomes deflected. As the current continues it will become deflected further and further, yet there will be a tendency to fall back into the original line of least resistance. The final form of the discharge will there-

fore not be one of equilibrium, but a compromise between the continuous rotation which the magnet tends to set up and the tendency to choose the path of least resistance. There is a real difference between this view and that generally brought forward; for, if I am correct, we should have in the final stage, which to us seems to be one of equilibrium, the particles of the gas carried through the current in a direction at right angles to it.

I think that I may quote the experiments of De la Rive on the rotation of a current round a magnet in support of what I have said. I have repeated his experiments by using a vessel very similar to those previously described: the inner cylinder contained the pole piece of a strong magnet, and was not used as electrode. One of the electrodes was a ring surrounding the axis; the other, a wire in the direction of the axis of the magnet. It has already been pointed out by De la Rive that the experiment is not successful with air; there seems a tendency towards rotation, but no rotation. Here, then, the preponderance of conductivity of the particles which have already carried the discharge does not seem sufficient to rotate the current; yet we cannot imagine that, for the same intensity of current, the effect of the magnet should not be the same. We must conclude, therefore, that here the particles are driven through the current, but do not carry the current with them. Even with vapours like alcohol, with which a continuous rotation can be obtained, it often happens that the current rotates only through a small angle, then suddenly jumps back into its original lines, and then tries to go round for some time, until it finally succeeds. Those who are familiar with the experiments of Plücker will find, I think, that they can easily be explained by what I have said, but that in no case can the form in which the discharge takes place be one of equilibrium; nor is it even a circle, which is the curve in which a flexible wire carrying the current would set if it was fixed at both ends.

As far as the effect of the magnet on the negative glow is concerned, it is generally considered sufficient to say that it sets in magnetic lines of force, or sometimes that it winds itself in spirals round those lines. The facts are true, and easily explained by any theory of projection, but they do not contain the whole truth.

In order to understand fully the action of the magnet, we have to be careful in distinguishing two totally distinct questions. The first question is this: In what way does the magnet affect the rays of the glow which start from any given part of the negative electrode? This question has been satisfactorily answered by means of the theory of projection. The second question, which has not received sufficient attention, is this: At what parts of a negative electrode placed in magnetic field does the glow form itself? For we find that large parts of a kathode sometimes remain absolutely dark in a magnetic

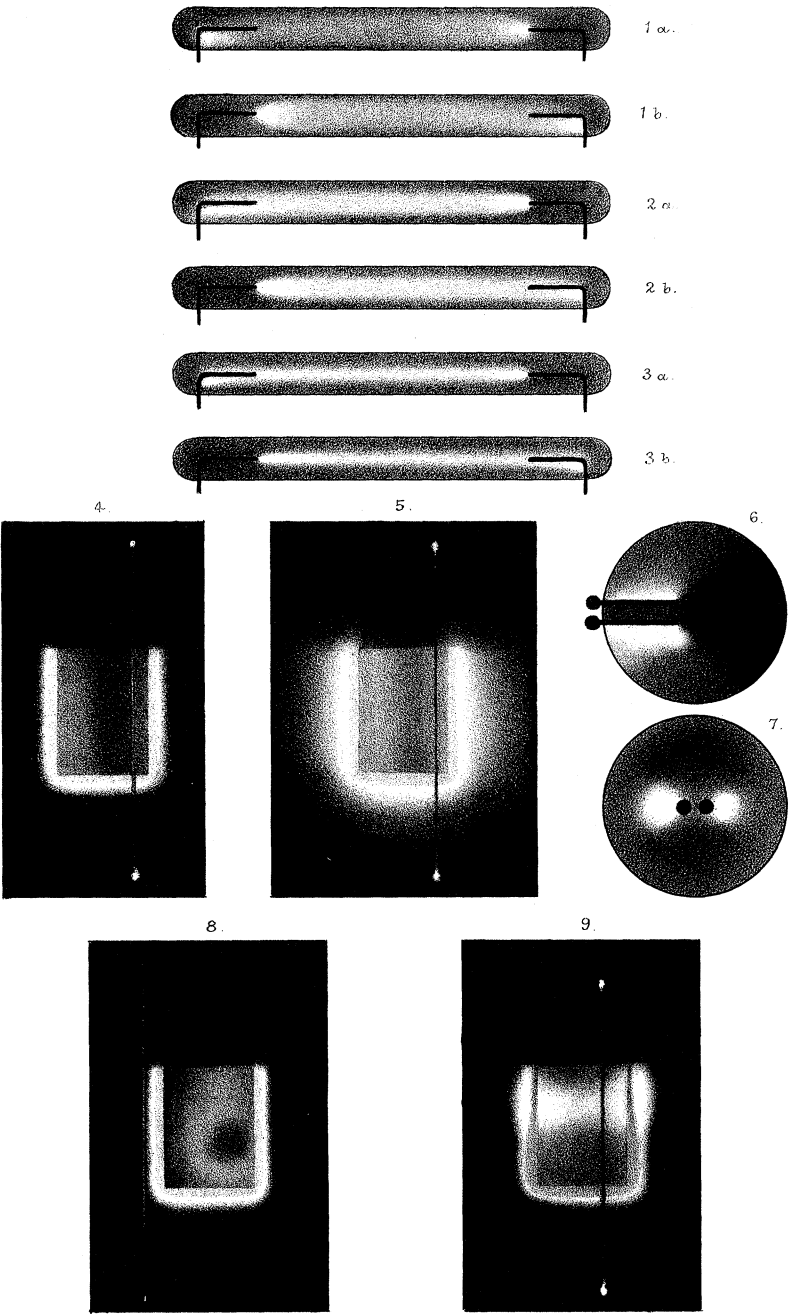
field, while they are covered with a glow on removal of magnetisation.

I have found the following explanation satisfactory in accounting for the phenomena observed by me or recorded by others. Suppose the whole negative electrode to be covered with the glow and then placed into the magnetic field. The negatively charged particles will be deflected in their path, and at some times they will tend to separate, at others they will be thrown together. Where they are thrown together the temperature will rise, and the discharge will pass more freely, and the current here will be strengthened, and the temperature still further increased. There is then, finally, a tendency of the glow to settle down *exclusively* at those places at which, owing to the effect of the magnet, the particles are thrown together. If in the vessel (fig. 1) a small electromagnet is introduced into the inner cylinder with its axis at right angles to the axis of the cylinder, it is found that the parts of the aluminium foil covering the two poles of the magnet are absolutely dark (fig. 8, Plate 1). It is clear that, if there was any glow at these parts, the particles carrying the current would be driven asunder, while they are thrown together near the middle parts of the magnet, where consequently the glow becomes strongest.

If into the same vessel we place a magnet longitudinally, the effect is that observed in fig. 9. Here again the glow settles round the centre of the magnet. The electromagnet used in this last experiment had a length of 8 centims., so that it filled completely the aluminium cylinder. That the question here introduced as to the parts of the cathode at which the glow chiefly settles is distinct from the more direct effect of the magnet on the glow, once that glow is formed, is clearly shown in cases where the vessel contains two negative electrodes, one of which only is affected by the magnet. I have used, for instance, a vessel containing two aluminium cylinders opposite each other. If a magnet is introduced into one of them, the glow will sometimes be taken away entirely from the other cylinder; a fact easily explained by the greater facility of the formation of the glow where the temperature is increased by a concentration of particles.

Fig. 9 also shows a curious effect of the magnet on the width of the dark space. Where the glow is strongest the dark space is very narrow, while it is widened wherever the glow is weak. It has been proved by Crookes that the dark space becomes narrower when the intensity of the current is increased, and the effect shown in the photograph is a simple consequence of this fact.

I have been during the whole of this investigation very ably assisted by Mr. Arthur Stanton; without his help I should not have been able to overcome the great practical difficulties which present themselves



when large vessels of complicated form, like those used by me, have to be put together and exhausted. All photographs were taken by him. I have also to acknowledge valuable assistance from Mr. Moss, a student at the Owens College.

“On the Experimental Determination of the Index of Refraction of Liquefied Gases.” By Dr. L. BLEEKRODE. Communicated by Dr. GLADSTONE, F.R.S. Received and read June 19, 1884.

I. Preliminary Remarks.

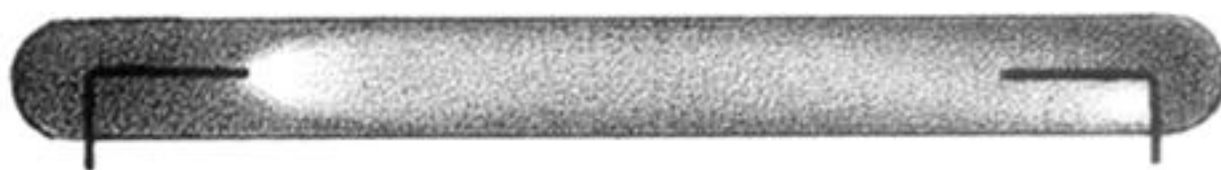
On a previous occasion* I had the honour to present to the Royal Society some results of an investigation made about electrical conductivity of chemical compounds, and I then chiefly examined the liquefied gases, pointing them out as very bad conductors. I have since been engaged in studying another property of these substances, and I have succeeded in determining in an experimental way their refractive power. As in England and abroad several papers have been subsequently published bearing on the relation between the liquid and gaseous conduction of matter, and especially liquefied gases present themselves well adapted to this kind of research, I hope the Royal Society will consider my paper not devoid of interest, the more so because our knowledge of their physical constants is somewhat limited. And though we possess numerous determinations of the refractive power of a vast number of chemical compounds, still increasing daily, I have found only very little information concerning my subject, this being limited to sulphurous and prussic acid, that are readily liquefied by cold and present no difficulty in manipulating. Faraday in his extensive paper on liquefied gases, published in 1823, when describing the properties of several of them, compares only their index of refraction to that of water, calling it more or less, and Brewster in 1826 mentioned in a communication to the Society of Edinburgh the index of refraction of liquefied cyanogen as 1.316, but without any remarks on the manner in which it was deduced.

I will commence this paper by describing the method I followed to obtain the numerical values of the index of refraction of several gases, liquefied either by pressure or by cold, and that enabled me to surmount the difficulties resulting from high tensions and small quantities of fluid substance, that may perhaps have kept back other experimenters from this field of research.

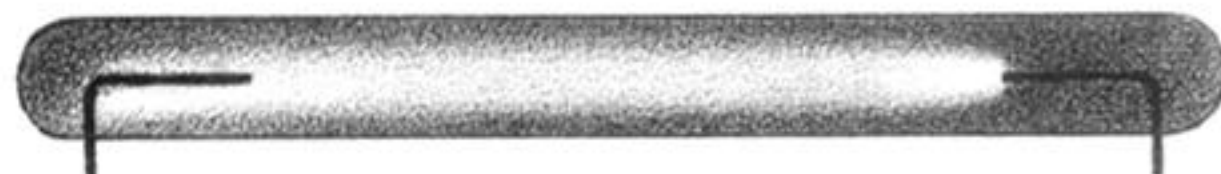
* “Proc. Roy. Soc.,” vol. 25, p. 322.



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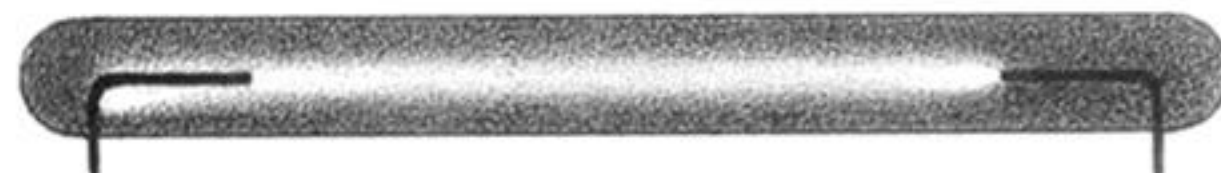
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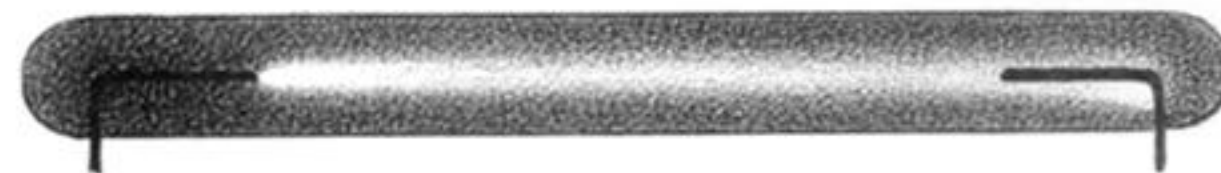
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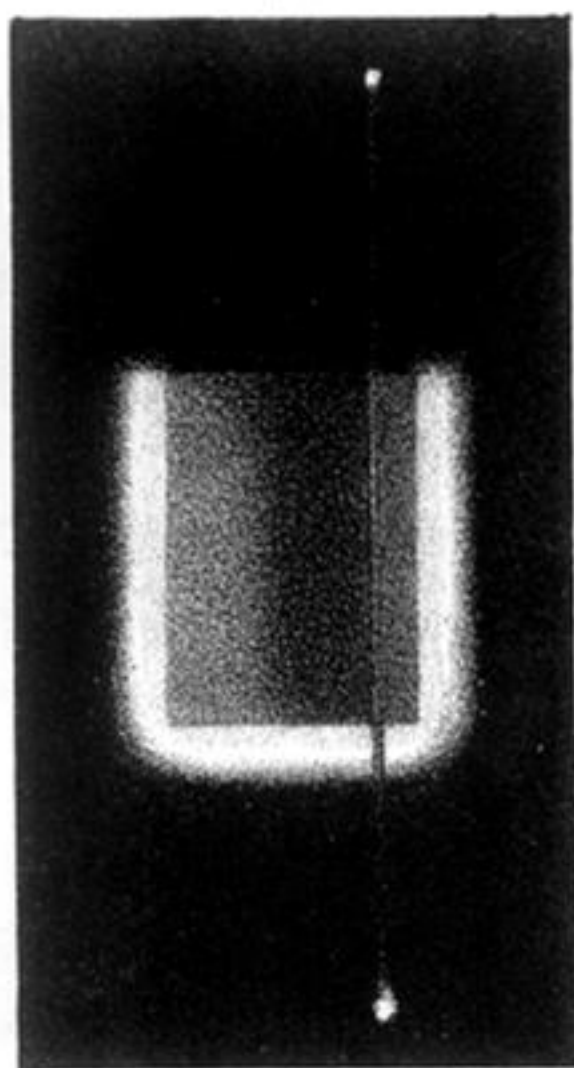


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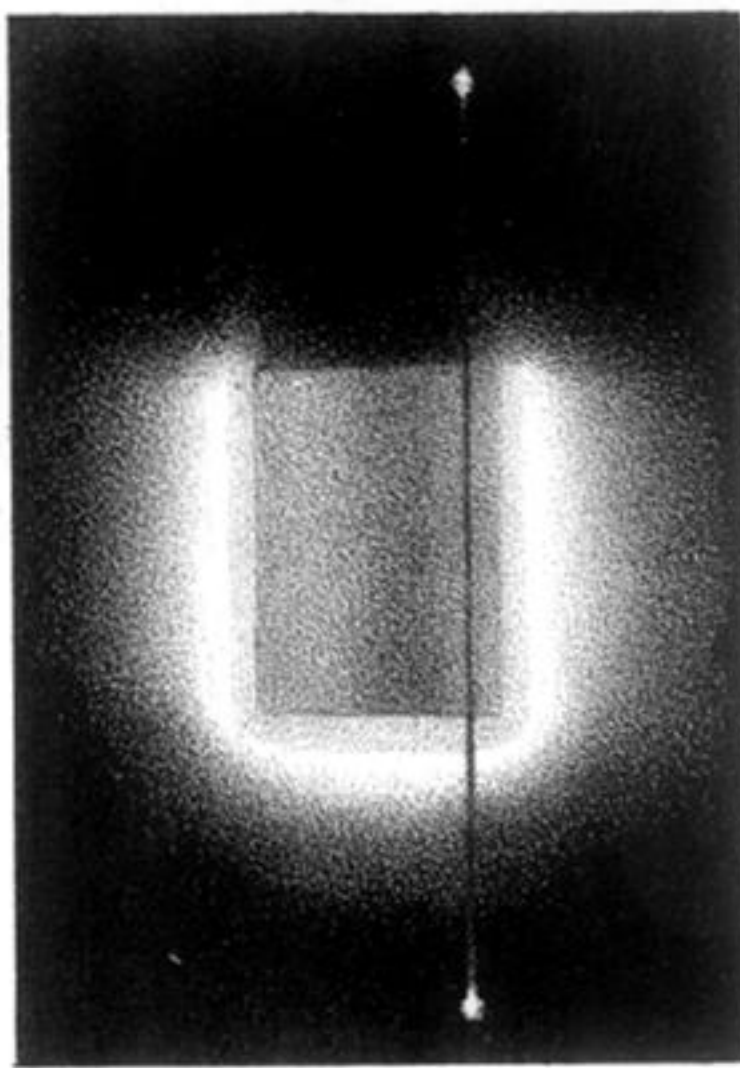


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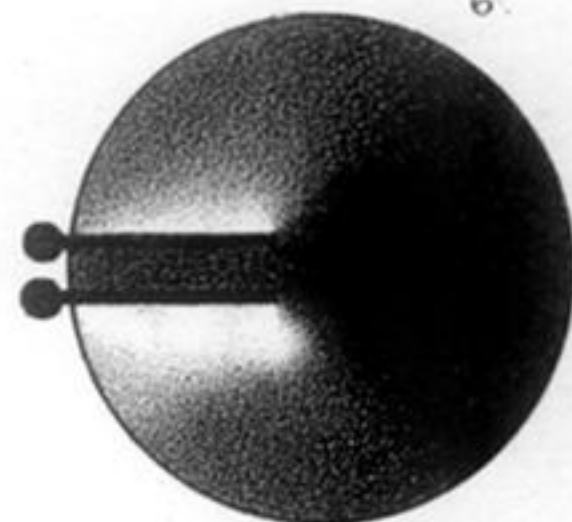
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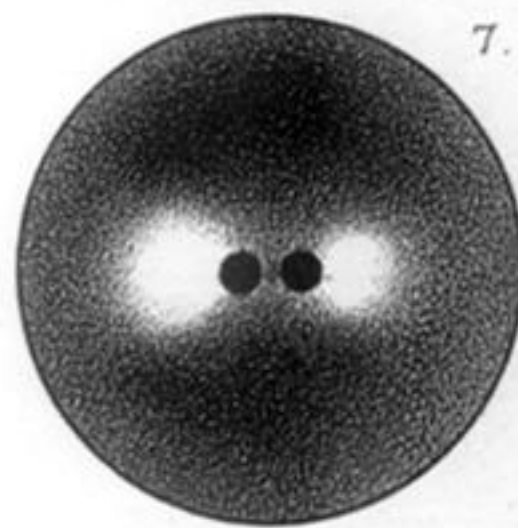
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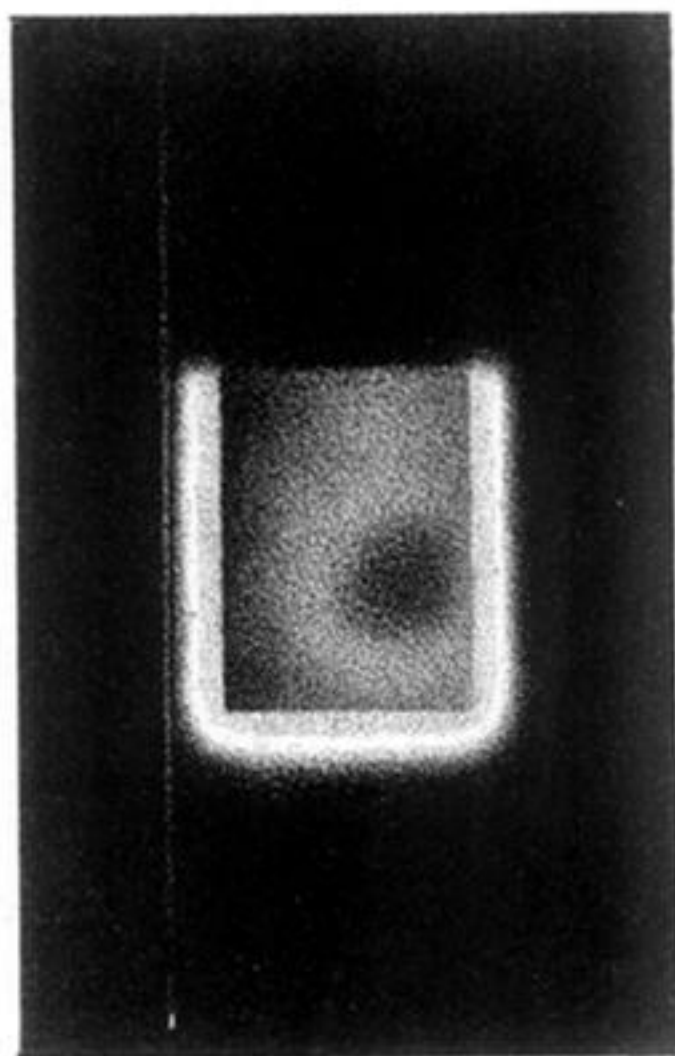
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