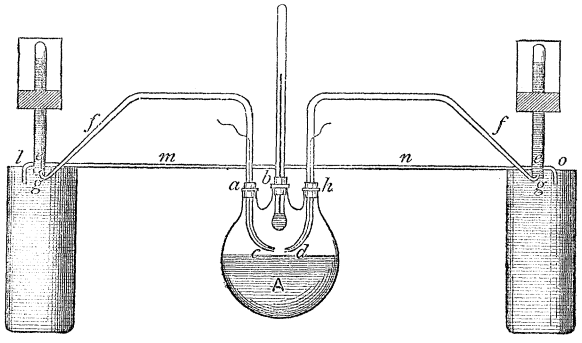
II. "The Electrolysis of Steam." By J. J. Thomson, M.A., F.R.S., Cavendish Professor of Experimental Physics in the University of Cambridge. Received February 18, 1893.

It is well known that steam is split up into hydrogen and oxygen when an electric discharge passes through it. A very careful examination of the laws of this phenomenon was made more than thirty years ago by Perrot;* as his results are very remarkable, and seem to be not at all well known, I will describe, as briefly as possible, his apparatus, and the results he obtained with it. The apparatus used by Perrot in his experiments is represented in fig. 1, taken from his paper. The spark passed between two platinum wires sealed into

Fig. 1.†



glass tubes, *cfg*, *dfg*, which they did not touch, except at the places where they were sealed; the open ends, *c*, *d*, of these tubes were about 2 mm. apart, and the wires terminated inside the tubes at a distance of about 2 mm. from the ends. The other ends of these tubes were inserted under test-tubes *e*, *e*, in which the gases, which passed up the tubes, were collected. The air was exhausted from the vessel A, and the water vapour through which the discharge passed was obtained by heating the water in the vessel; special precautions were taken to free this water from any dissolved gas. The stream of vapour arising from this water drove up the tubes the gases produced by the passage of the spark; part of these gases was produced along the length of the spark. Part of the gases so collected has been decomposed by causes which would not be affected by reversing the electrical conditions of the electrodes, *e.g.*, by such causes as the heat

* 'Annales de Chimie et de Physique' [3], vol. 61, 1861, p. 161.

† From 'Notes on Electricity and Magnetism' (Clarendon Press, Oxford).

produced by the sparks. We should not expect to find any simple relation between the amount of decompositions from these causes and the quantity of electricity which had passed through the gas. The hydrogen and oxygen produced by such causes would, however, be driven up the tube in chemically equivalent proportions, and could therefore be eliminated by sending a spark through these gases, when they would recombine and form water.

When the sparking had ceased, the gases which had collected in the test-tubes *e* and *e* were analysed; in the first place they were exploded by sending a strong spark through them; this at once got rid of the hydrogen and oxygen which existed in chemically equivalent proportions, and thus get rid of the gas produced by heat, &c., along the length of the spark. After the explosion, the gases left in the tubes were the hydrogen or oxygen in excess, together with a small quantity of nitrogen, due to a little air which had leaked into the vessel in the course of the experiments, or which had been absorbed by the water. The results of these analyses showed that there was always an excess of oxygen in the test-tube in connexion with the positive electrode, and an excess of hydrogen in the test-tube connected with the negative electrode, and, also, that the amounts of oxygen and hydrogen in the respective tubes were very nearly chemically equivalent to the amount of copper deposited from a solution of copper sulphate in a voltameter placed in series with the discharge tube.

The results of some of Perrot's experiments are shown in the following table :—

Duration of experiment.	Weight of Cu deposited in voltameter and its equivalent in c.c. of H.	Excess of H in tube next − electrode.	Excess of O in tube next + electrode.
4·0 hours	8·5 mgm. Cu; 3·00 c.c. H	3·00 c.c.	1·40 c.c.
4·0 „	6·0 „ 2·12 „	2·10 „	0·95 „
3·0 „	5·5 „ 0·94 „	1·80 „	0·85 „
3·5 „	6·0 „ 2·12 „	2·05 „	0·90 „

Thus in Perrot's experiments the excess of hydrogen appears at the negative electrode, the excess of oxygen at the positive, and these excesses are very nearly chemically equivalent to the amount of Cu deposited in a copper sulphate voltameter placed in series with the discharge tube. Ludeking* confirmed the result that when sparks pass through steam there is an excess of oxygen at the positive, and of hydrogen at the negative, electrode.

As these results bear very closely on the method by which the dis-

* 'Phil. Mag.' [5] vol. 33, 1892, p. 521.

charge passes through gases, and seem to have special reference to a view which I have long held, that the discharge through gases is accompanied by chemical changes analogous to those which take place in electrolytes conveying currents, I was anxious to repeat and, if possible, extend them. On attempting to do this, I met with very considerable difficulties, and it has taken more than a year's work to overcome these, and to arrange the experiments so as to get definite and consistent results. For this reason, as well as from the fact that my results differ very materially from those obtained by previous experimenters, I shall enter at greater length into the details of the experiments than would otherwise be necessary.

The form of apparatus which I now use, though similar in its main features to that used by Perrot, differs from it in some respects. Before describing the apparatus in detail, I will indicate the chief points of difference between it and Perrot's.

One source of doubt in Perrot's experiment seemed to me to arise from the proximity of the tubes surrounding the electrodes to the surface of the water, These tubes were narrow, and, if they got damp, the sparks, instead of passing directly through the steam, might conceivably have run from one platinum electrode to the film of moisture on the adjacent tube, then through the steam to the film of moisture on the other tube, and thence to the other electrode. If anything of this kind happened, it might be urged that, since the discharge passed through water in its passage from one terminal to the other, some of the gases collected in the tubes might have been due to the decomposition of the water and not to that of the steam. To overcome this objection, I have (1) removed the terminals to a very much greater distance from the surface of the water, and placed them in a region surrounded by a ring burner, by means of which the steam can be heated to a temperature of 140° or 150° C.; (2) I have got rid of the narrow tubes surrounding the electrodes altogether by making the tubes through which the steam escapes partly of metal, and using the metallic parts of these tubes as the electrodes.

Though I prefer this method of arranging the electrodes as being somewhat more convenient than Perrot's form of the experiment, in which the electrodes were wires surrounded by glass tubes, I have repeated the experiments described below, using wire electrodes; the results, however, were precisely the same as those obtained when the tubular electrodes were used. One great advantage of these tubular electrodes is that the quantity of metal in them is large enough to keep them quite cool during the discharge; while, when wire electrodes are used, the end of the negative terminal becomes red hot if any considerable current passes through the steam.

Instead of following Perrot's plan of removing the mixed gases from the collecting tubes *e*, *e*, fig. 1, and then exploding them in a

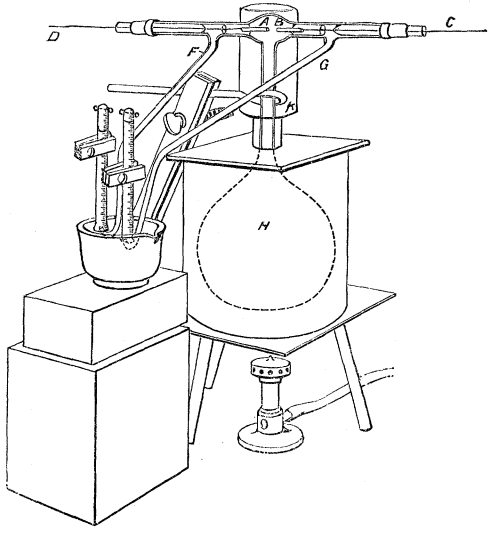
different vessel, I have collected the gases on their escape from the discharge tube in graduated eudiometers provided with platinum terminals by means of which the mixed gases were exploded *in situ* at short intervals during the course of the experiments. This plan avoids the trouble, waste of time, and risk of error incurred in moving the mixed gases from the collecting tube to the eudiometer. Its greatest advantage, however, is that it enables us to see with very little delay at which terminals the excesses of hydrogen and oxygen are appearing. As I shall have to explain below, the sides at which the excesses of hydrogen and oxygen appear can be reversed by altering the character of the spark, and it very much facilitates the investigation of the laws of this reversal to be able to tell, with as little loss of time as possible, at which terminal the excess of hydrogen is appearing.

Description of the Apparatus.

I will now pass on to describe the form of apparatus which, after many trials, was found to be the most convenient.

This is represented in fig 2. H is a glass bulb, 1·5 to 2 litres in volume, containing the water which supplies the steam. A tube, L, about 0·75 cm. in diameter and 35 cm. long, is joined on to this. In many cases this was *fused* directly on to the bulb; I do not think, however, that this is necessary, and I have found no ill effects arise from

FIG. 2.

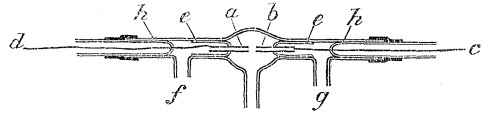


making this connexion by placing a rubber stopper in the prolongation of the bulb, and pushing the tube L through a hole in this stopper, care being taken to push the tube right through the hole. I may remark in passing that it is very desirable to adopt a form of apparatus which is easily constructed; the life of these tubes is by no means long, as they are exceedingly liable to crack, especially when cooling, at the end of an experiment. The apparatus I am now describing is one which was designed with special reference to easy construction, and fused joints are done away with in those places where I have found by experiment that this course could be taken without injury to the accuracy of the experiments. I have, however, repeated the experiments, using apparatus in which all the joints were fused.

The top of the tube L is fused on to the horizontal discharge tube CD; this tube is blown out into a bulb in the region where the sparks pass, so that when long sparks are used they may not fly to the sides of the tube. The top of the tube L, near its junction with CD, is encircled by a ring burner K, and this part of the tube is surrounded by an asbestos case; by these means the steam may be superheated to a temperature of 140° to 150° C.

The details of the electrodes between which the sparks pass are shown in fig. 3. For the metal parts *a*, *b*, it is necessary to use some metal which is not oxidised by the steam, as a very small amount of oxidation would be sufficient to render the results nugatory.

Fig. 3.



I have used as the electrodes, (*a*) brass tubes thickly coated with gold with their sparking ends carefully rounded off, or (*b*) tubes made by winding thick platinum wire up into a coil. These tubes are placed in pieces of glass tubing, *e*, *e*, to hold them in position. To facilitate the expulsion of air from the apparatus, it is desirable that the metal tubes should not fit so tightly into the glass ones as to prevent the steam from passing between the two. If they fit too tightly to allow this, air is apt to lodge between the metal and glass tubes, and if this gets driven out into the delivery tubes F, G (fig. 2) when the sparks pass, it will vitiate the experiment.

The glass tubes *e*, *e* stop short of the places *f*, *g*, where the delivery tubes join the discharge tube. The discharge tube is closed at the ends by two pieces of tube, *h*, *h*, which have their ends inside the tube

fused up; wires connected to the electrodes *c*, *d* are fused through the closed ends of these tubes. It is desirable that the closed ends of the tubes *h*, *h* should come up as close as possible to the exits *f*, *g*, as air is very apt to remain in the tube if there are any places through which the steam does not rush. The tubes *h*, *h* may either be fused on to the spark tube or fastened to it by rubber tubing.

The delivery tubes F, G (fig. 2) are fused on to the discharge tube at *f*, *g* (fig. 3). These tubes are about 5 cm. in diameter and terminate in narrow openings. It is essential that the steam and the mixed gases should escape through the tubes F, G at approximately the same rate; to ensure this, the narrow extremities of these tubes should be equal both in length and width. This was attained by drawing out a piece of tubing which was originally of the same diameter as F, G, and then cutting it at the middle of the narrow part; the two halves were then either fused or fastened by rubber tubing to F, G. The narrow ends of F, G are turned up and placed under mercury in the vessel M (fig. 2). Over these ends, graduated eudiometer tubes are placed; these are filled with mercury at the beginning of the experiment, but the mercury soon gets displaced by the water produced by the condensation of the steam rushing through the tubes.

The heat produced by this condensation serves a useful purpose; it raises the temperature of the water in the eudiometer tubes over which the gases are collected to over 80° C., and thus, since hot water absorbs oxygen but not hydrogen much less readily than cold, diminishes the disturbing effect due to the greater absorption of the oxygen than of the hydrogen by the water over which the gases are collected.

The effect produced by electrification on the condensation of a jet of steam is shown in a very striking way by this apparatus. When the delivery tubes are open to the air, the steam, after escaping from the nozzles, goes some inches before it condenses sufficiently to form a cloud; as soon, however, as the coil is turned on and the sparks pass, brownish clouds reaching right down to the nozzles are at once formed. The cloud is denser in the steam which has gone past the negative electrode than in that which has gone past the positive.

Precautions which it is necessary to take to ensure Correct Results.

These can, perhaps, best be realised by considering that what we have to measure is the excess of hydrogen or oxygen, as the case may be, left after exploding the mixed gases. Now, if we consider, firstly, that this excess is a small fraction of the original volume of the mixed gases—the exact proportion between the two varies greatly with the length of the spark, but in some cases the excess did not amount to more than 5 per cent. of the mixed gases; secondly, that only a very small portion of the steam passing through the

discharge tube is decomposed by the spark, so that the volume of the mixed gases bears a very small proportion to that of the steam—certainly nothing like 1 : 100 in my experiments—it is evident that if the steam contains anything like 1/10 per cent. of air, the oxygen in this air will be comparable with that produced by the sparking, and its presence will prevent any reliable results being obtained.

This air may come from two sources—(1) it may be present in the tube originally; and (2) it may have been absorbed by the water.

To get rid of the air from the first source, the tube was so constructed that there were no blind alleys; every part of it was a thoroughfare for the steam. In addition to this, the vessel H (fig. 2) was, at the beginning of the experiment, filled so full of distilled water, by dipping one of the delivery tubes under the water and connecting the other to a water pump, that when the water was heated its expansion was sufficient to cause it to fill the whole of the tube and overflow.

To get rid of the air dissolved in the water, I found no plan so efficacious as prolonged boiling. In the earlier experiments, in addition to the boiling, I tried to absorb the oxygen by mixing oxidising agents with the water; finally, however, I dispensed with these and trusted entirely to the boiling to remove the air.

The distilled water was boiled vigorously for six or seven hours with the ends of the tubes F, G open to the atmosphere. The eudiometer tubes filled with mercury were then placed over the ends of the delivery tubes F, G, so that, if any air were mixed with the steam, it would be collected in these tubes. The steam was then allowed to run into the eudiometer tubes for about an hour, when the tubes were examined to see if they contained air. If any air was observed, the eudiometer tubes were removed and vigorous boiling maintained until, on repeating the experiment, the air was found to have disappeared.

As the excess of hydrogen obtained in the hour by sparking through the steam would have been at least 1 c.c., and in many experiments much more, while the air did not form a bubble large enough to be visible, we may, I think, conclude that there was not enough air present to affect the result appreciably.

Method of Producing the Sparks.

The sparks were produced by means of a large induction coil, which would give sparks about 5 cm. long when the current from five large storage cells, which was the usual battery power employed, was sent through it. The break used was, generally, the ordinary electro-magnetic break supplied with these coils, but in some experiments a slow mercury break was employed.

On trying to use the coil in the ordinary way, the current obtained was exceedingly small, so small that the hydrogen liberated in a water voltameter placed in series with the discharge tube only amounted to about 0·25 c.c. per hour. As it is inconvenient to work with such small currents, on account of the time which has to elapse before a quantity of gas can be obtained sufficient to enable accurate measurements to be taken, I endeavoured to increase the current from the coil. I found that, as I believe is the case with all induction coils, the condenser supplied with it had not nearly enough capacity to enable the coil to give out its maximum current. When I added to this condenser a large paraffin paper one, with a capacity of about 6 micro-farads, the current from the coil was increased more than twenty times, and I found no difficulty in getting from 4 to 6 c.c. of hydrogen liberated per hour in the water voltameter in series with the discharge tube.

In order to measure the quantity of electricity which passes through the spark tube, a well-insulated water voltameter was placed in series with it, and the quantity of hydrogen liberated in this voltameter observed. The gases liberated in this voltameter were repeatedly tested, in order to see whether there was any mixing up of the hydrogen and oxygen in the collecting tubes over its electrodes. Such admixture seemed possible, as the electromotive force produced when the circuit is "made" is in the opposite direction to that produced when it is broken. The test consisted in vigorously sparking through the gases collected in the voltameter, but no contraction occurred. As, however, it is very difficult to get a mixture of hydrogen and oxygen to explode if the hydrogen is greatly in excess, I added to the hydrogen in the voltameter enough oxygen to cause an explosion; the contraction in this case corresponded to the oxygen added, showing that there was no oxygen originally present. We may therefore conclude that the current sent through the secondary circuit on "making" the coil is in this case too small, in comparison with that produced on "breaking" the circuit, for its effects to be appreciable.

Method of Making the Experiments.

After it had been ascertained, in the way previously described, that all the air had been expelled from the vessel, the eudiometer tubes were filled with mercury and placed over the ends of the delivery tubes, and the spark tube connected up with the coil.

The next step was to see if the rates of flow through the delivery tubes were approximately equal. This was done by turning on the coil and collecting the mixed gases in the eudiometer tubes; if the volume of these gases in the two tubes was not the same, the appa-

ratus had to be readjusted. When everything was fused together, and there were no flexible joints, this had to be done by letting the delivery tubes F, G dip into separate basins filled with mercury, and then to raise or lower the level of the mercury in one or other of these basins until the rates of flow of the gases into the two eudiometer tubes were approximately equal.

It is not, however, necessary to have two vessels if the narrow portions of the exit tubes are connected with the main portions by flexible rubber joints turned under the surface of the mercury, as in this case it is very easy to raise or lower the end of one or other of the tubes without interfering with the rest of the apparatus.

These flexible connexions do not, as I have found by direct experiment, introduce any source of error, and add greatly to the longevity of the tube. When everything is fused up and the connexions are rigid, the shocks due to the explosion of the mixed gases are exceedingly liable to break the exit tubes from off the main tubes, while they are comparatively harmless when there is a flexible connexion between the piece of the exit tube immediately under the collecting tube and the rest of the apparatus.

When the exit tubes had been adjusted so that the rates of flow through the two tubes were the same, the mixed gases were emptied out of the collecting tubes, which were refilled with mercury; the water voltameter was placed in series with the steam tube, and the coil again set in action.

The steam which came up the collecting tubes condensed into hot water which soon displaced the mercury; the mixed gases collected over this hot water, and were exploded at short intervals of time by sparks from a small Wimshurst machine. The gases did not disappear entirely when the sparks passed; a small fraction of the volume remained over after each explosion, and the volume which remained was greater in one tube than in the other.

The residual gas which had the largest volume was found on analysis to be hydrogen; the other was oxygen. Thus, by comparing the volumes of the residual gases in the two tubes it could readily be ascertained next to which electrodes the excesses of hydrogen and oxygen were appearing.

There are other differences in the behaviour of the gases in the two tubes which, though less obvious than the difference in volume, are quite as characteristic. One of these is the difference in the ease with which explosions take place; the gases explode much more readily on the side at which the oxygen is in excess than on the other. Another very characteristic difference is that when sparks pass in rapid succession through the tube in which the oxygen is in excess bright spangles often appear floating about in the gas, due, I imagine, to the ignition of small pieces of platinum torn from the

electrodes. I have never observed these spangles on the hydrogen side.

When a sufficient quantity of the residual gas had been collected, which generally happened when the sparks had been passing for an hour or an hour and a half, a considerable volume of the mixed gases was allowed to accumulate, so as to make sure of an explosion when the spark from a Wimshurst passed through them. The coil was then stopped and the mixed gases exploded, and the quantity of hydrogen in the water voltameter determined.

The residual gases in the collecting tubes were then analysed; the first step was to cool these gases, which while the steam had been rushing into the tubes had been at a temperature of more than 80° C., down to the temperature of the room. After this had been done, the nature of these gases was determined by adding known volumes of oxygen and hydrogen, prepared electrolytically from water, and observing the contraction which took place when a spark passed; the addition of the hydrogen or the oxygen, as the case might be, was continued until no further contraction took place on sparking.

The result of these analyses was that when the sparks were not too long the residual gas in one tube was found to be pure hydrogen, that in the other pure oxygen; if any other gases were present their volume was too small to be determined by my analysis. This result was only attained after considerable experience with the experiments and with the precautions necessary to obtain correct results; in the earlier experiments there was always a considerable quantity of some other gas (which, I suppose, was nitrogen) present.

When the sparks passing through the steam were very long I never succeeded in getting rid of this nitrogen; indeed, in some cases it amounted to more than 30 per cent. of the oxygen. I am not sure what the source of this nitrogen is; it may have been absorbed by the electrodes and given out when the sparks pass, or it may have come from the walls of the discharge tube, as these long sparks have a tendency to occasionally jump to the walls, and when they do so they may liberate air which would otherwise adhere to the glass.

Results.

The results obtained by the preceding method varied greatly in their character with the length of the spark; I shall therefore consider them under the heads "short sparks," "medium sparks," and "long sparks."

The lengths at which a spark changes from "short" to "medium," and then again to "long," depend on the intensity of the current passing through the steam, and therefore upon the size of the induction coil and the battery power used to drive it. The limits of

"short," "medium," and "long sparks" given below must therefore be understood to have reference to the particular coil and current used in these experiments. With a larger coil and current these limits would expand; with a smaller one they would contract.

Short Sparks.

I shall begin by describing the experiments with short sparks, *i.e.*, sparks from 1·5 to 4 mm. long. Here the appearance of the spark shows all the characteristics of the "arc" discharge.

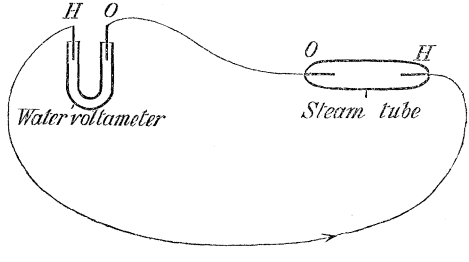
The discharge passes as a thickish column with ill-defined edges, and when placed in a wind it is blown out to a broad flame-like appearance.

For these short sparks or "arcs," as I prefer to call them, two very important laws were found to be true—

1. That within the limit of error of the experiments the volumes of the excesses of hydrogen in the one tube, and of oxygen in the other, which remain after the explosion of the mixed gases, are, respectively, equal to the volumes of the hydrogen and oxygen liberated in the water voltameter placed in series with the steam tube.
2. The excess of hydrogen appears in the tube which is in connexion with the *positive* electrode, the excess of oxygen in the tube which is in connexion with the *negative* electrode.

The second of these results surprised me very much when I first observed it, as both Perrot and Ludeking had found that in the electrolysis of steam, as in that of water, the excess of hydrogen was at the negative and that of oxygen at the positive electrode. According to my experiments, however, the electrode at which the hydrogen appears in the electrolysis of steam is of the opposite sign to that at which it appears in the electrolysis of water. So that, if a water voltameter is placed in series with the steam tube, the gases are liberated in the way shown in the accompanying diagram (fig. 4), in

FIG. 4.



which it will be seen that the electrodes at which the hydrogen appears are next each other, as are also those at which the oxygen appears, instead of being arranged alternately as they would have been if two water voltameters had been placed in series.

A very large number of experiments were made to test the truth of this law, platinum as well as gold electrodes were tried, and I replaced the metal tubes which serve as the electrodes in my apparatus by wires surrounded by glass tubes; so as to make the form of the apparatus approximate as closely as possible to that used by Perrot; the results, however, were all perfectly definite and uniform; the hydrogen always appeared in the tube next the positive electrode, the oxygen in the one next the negative electrode.

A good method of showing the way in which the hydrogen follows the positive electrode is to keep the coil on one way until about 2 c.c. of hydrogen have been collected in the tube next the positive and about 1 c.c. of oxygen in the tube next the negative electrode, then reverse the coil; the volume of residual gas will be found gradually to diminish as the mixed gases are exploded, and this diminution goes on until the hydrogen and oxygen previously collected have quite disappeared, and the water reaches right to the top of the collecting tubes. After this, if the sparking is continued, oxygen begins to appear where hydrogen had previously been, and *vice versâ*.

The reversal of the coil supplies a very useful means of telling whether the apparatus is properly adjusted. If the rates of flow through the two delivery tubes are very different, hydrogen may appear in one of the tubes, and oxygen in the other, from some cause which is not electrical; this can be detected at once by reversing the coil.

The following table (p. 102) contains the results of some measurements of the relation between the excesses of hydrogen and oxygen in the collecting tubes attached to the steam tubes and the quantity of hydrogen liberated in a water voltameter placed in series with the discharge tube. The ordinary vibrating break supplied with induction coils was used, except when the nature of the break is indicated.

The results tabulated above show that the excesses of hydrogen and oxygen are approximately equal to the quantities of hydrogen and oxygen liberated in the voltameter.

Medium Sparks.

When the spark length is greater than 4 mm., the first of the preceding results ceases to hold. The second of these, that the hydrogen comes off at the positive electrode, remains true until the sparks are some 11 mm. long; but, instead of the hydrogen from the steam being

Spark length in millimetres.	Metal used for electrodes.	Excess of H in tube next + electrode.	Excess of O in tube next − electrode.	H in water voltameter.	Duration of experiment in minutes.
		c.c.	c.c.	c.c.	
1·5	gold	3·25	1·5	3·2	40
1·5	platinum	2·8	1·6	3·0	30
1·5	gold	1·7	0·8	1·8	20
2·0	gold	2·0	1·08	1·95	30
2·0	gold	3·25	1·75	3·2	60
2·0	platinum	1·8	tube broken	2·0	not noted
2·0	platinum	3·0	1·5	3·0	60
2·0	gold	2·5	1·5	3·0	60
3·0	gold	1·8	not noted	1·8	not noted
3·0*	gold	0·7	0·4	0·8	90
3·0†	gold	1·6	not noted	1·75	not noted
4·0	gold	0·9	0·37	0·7	20
4·0	gold	2·75	1·25	2·7	60
4·0†	gold	1·0	not noted	1·25	not noted
4·0	gold	2·5	1·25	2·3	45

equal to that from the water, it is, when the increase in the spark length is not too large, considerably greater.

The following are a few instances of this :—

Spark length.	Hydrogen from steam.	Hydrogen from voltameter.
5 mm.	1·8	1·2
5 ,,	3·75	3·0
5 ,,	4·4	2·1
6 ,,	4·0	1·6
7 ,,	4·25	3·0
7 ,,	3·75	2·0
8 ,,	3·75	2·6

This increase in the ratio of the hydrogen from the steam to that from the voltameter does not continue when the length of the spark is still further increased. When the spark length has got to 8 mm. this ratio begins to fall off very rapidly as the spark length increases, and we soon reach a spark length at which it seems almost a matter of chance whether hydrogen or oxygen appears in the collecting tube connected with the positive electrode.

When the sparks are at this critical length the kind of thing which happens is somewhat as follows :—For some time an excess of hydrogen (say) comes off in the tube next the positive electrode, and accumulates as the mixed gases are exploded; then some slight

* In this experiment a slow mercury break making about four breaks per second was used.

† In these experiments large Leyden jars were attached to the electrodes.

change takes place in the action of the coil, and an excess of oxygen begins to appear; this gradually wipes out the accumulation of hydrogen, and if it goes on long enough makes the residual gas in the tube entirely disappear; then the oxygen begins to accumulate, only, however, to be wiped out later, when another change in the action of the coil has caused hydrogen to appear in excess in this tube. Thus, in this case, the residual gas in the tube does not, as before, steadily increase with the time of sparking, but is continually waxing and waning, sometimes being oxygen and sometimes hydrogen.

Long Sparks.

When the spark length is increased beyond the critical value the excess of hydrogen, instead of appearing as with shorter sparks at the positive electrode, changes over to the *negative;* the excess of oxygen at the same time going over from the negative to the positive electrode. Thus the gases when the spark length is greater than its critical value, appear at the same terminals as they do when released from an ordinary electrolyte, instead of at the opposite terminals, as they do when the sparks are shorter.

The length of spark at which this reversal takes place depends, to a very great extent, upon the current sent through the steam: the smaller the current the shorter the critical spark length. By diminishing the current by inserting a liquid resistance I reduced, on one occasion, the critical spark length from 11 to 8 mm. This critical length, too, seems to depend upon a number of small differences not easily specified; it will even vary greatly in the course of one afternoon, though apparently nothing has been changed. I have found, however, that this capriciousness disappears either altogether, or to a very great extent, if Leyden jars—very small ones will do—are attached to the terminals of the steam tube, or if an air break is placed in series with that tube. Under these circumstances the critical length will, if the same coil is used, remain constant from day to day.

It will be noticed that my results, when the length of the spark is greater than the critical length, agree with those obtained by Perrot and Ludeking, as these observers found that the hydrogen appeared at the negative, the oxygen at the positive, electrode. Ludeking worked with long sparks only, so that his results are quite in accordance with mine. In Perrot's experiments the spark length was about 6 mm. I have never been able to reduce the critical length quite as low as this, even though I diminished the current to the magnitude of that used by Perrot; I have, however, got it as low as 8 mm., and it is probable that the critical length may not be governed entirely by the current.

I was not able to detect any change in the appearance of the spark as the spark length passed through the critical value. My observation on the connexion between the appearance of the discharge and the electrode at which the excess of hydrogen appears may be summed up in the statement that when the discharge is plainly an arc the hydrogen appears at the positive electrode, and when the hydrogen appears at the negative electrode the discharge shows all the characteristics of a spark. However, before the spark length reaches its critical value the discharge looks much more like a spark than an arc.

With regard to the quantity of hydrogen liberated from the steam in comparison with that set free in the voltameter, I find that when the spark length is a few millimetres greater than the critical length the amount of hydrogen from the steam is very approximately the same as that in the voltameter. The following table contains a few measurements on this point:—

Spark length.	Hydrogen from steam.	Hydrogen from voltameter.
10 mm.	0·7 c.c.	0·8 c.c.
12* ,,	0·75 ,,	0·9 ,,
14 ,,	0·8 ,,	1·1 ,,

When the sparks are longer than 14 mm. the amount of hydrogen from the steam was no longer equal to that from the voltameter. The results, however, were irregular, and, as mentioned before, there was a considerable quantity of nitrogen (?) mixed with the hydrogen and oxygen.

When the sparks are very much longer, say about 22 mm., the electrode at which the hydrogen appears reverses again, *i.e.*, the hydrogen comes off at the positive electrode, just as it does when the sparks are very short. With these very long sparks the current is extremely small, and it takes several hours to liberate 1 c.c. of hydrogen in the voltameter.

The proportion of hydrogen from the steam to that from the voltameter was with these long sparks too irregular to admit of any conclusions being drawn.

The preceding results show that in the electrolysis of steam, as in that of water, there is a very close connexion between the amounts of hydrogen and oxygen liberated at the electrodes and the quantity of electricity which has passed through the steam, and that this relation for certain lengths of sparks is the same in steam as in electrolytes. There is, however, this remarkable difference between the electrolysis of steam and that of water, that whereas in the case of

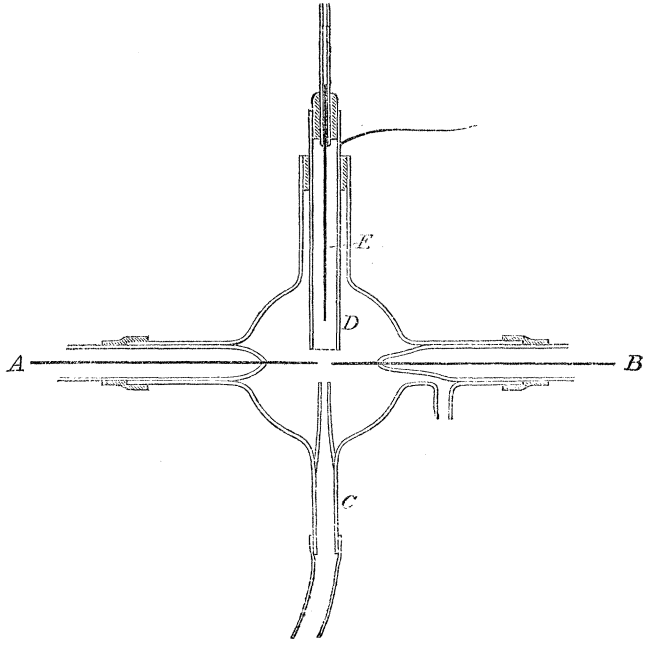
* In this experiment there was an air break 9 mm. long in series with the steam tube.

water the hydrogen always comes off at the negative, the oxygen at the positive, electrode, in the case of steam the hydrogen and oxygen come off sometime at one terminal, sometimes at the other, according to the nature of the spark.

The result obtained with the arc discharge, viz., that the oxygen appears at the negative electrode, the hydrogen at the positive, is what would happen if the oxygen in the arc had a positive charge, the hydrogen a negative one. As this is contrary to the commonly received views of the electro-chemical properties of these gases, I endeavoured to see if I could obtain any other indications of this peculiarity. With this object I have made a series of experiments on the properties of various gases when the arc discharge passes through them. I began these merely with the idea of elucidating the particular point mentioned above, but one experiment has led on to another until they form a series too long to be described here; I shall, therefore, limit myself to those experiments which seem to have the most direct bearing on the electrolysis of steam.

The apparatus used for these experiments is represented in the figure. The arc discharge between the platinum terminals A, B was produced by a large transformer, belonging to the Cavendish Labora-

FIG. 5.



tory, which transforms up in the ratio of 400 to 1; an alternating current of about 35 ampères, making 80 alternations per second, was sent through the primary of this. A current of the gas under examination entered the discharge tube through the tube C, placed underneath the arc, and blew the gas in the neighbourhood of the arc against the platinum electrode E, which was connected to one quadrant of an electrometer, the other quadrant of which was connected to earth. To screen the electrode E from external electrical influence, it was enclosed in a platinum tube, D, the end of which was made of fine platinum wire gauze, which, though it served as a screen for electrostatic action, yet allowed the gases in the neighbourhood of the arc to pass through it. This tube was connected to earth. After passing out of the tube, the electrode E was attached to one end of a gutta-percha-covered wire wound round with tin-foil connected to the earth; the other end of this wire was connected to the electrometer.

The experiments were of the following kind:—The quadrants of the electrometer were charged up by a battery; the connexion with the battery was then broken, and the rate of leak observed. When the arc was not passing the insulation was practically perfect, the spot of light reflected from the mirror of the electrometer hardly moving appreciably in the course of three minutes. As soon, however, as the arc was started, and for as long as it continued, the insulation of the gas surrounding E in many cases completely gave way. There were, however, some remarkable exceptions to this, which we now proceed to consider.

Oxygen.

We shall begin by considering the case when a well-developed arc passes through oxygen:—

1. When the electrode E is charged negatively. In this case it loses its charge very rapidly, it does not, however, remain uncharged, but acquires a positive charge, increasing until the electrode E has acquired a potential V. V depends greatly on the size of the arc and the proximity of the electrode; in many of my experiments it was from 10 to 12 volts.
2. When the electrode is charged positively. If the potential is very high, the electrode leaks until the potential sinks to V; after reaching this potential the leak stops, and the gas seems to insulate as well as when no discharge is passing through it. If the potential to which E is initially raised is less than V (a particular case being when the electrode is entirely without charge to begin with), the positive charge increases until the potential of E rises to V.

Thus we see (1) that an electrode immersed in the arc oxygen can

insulate a small positive charge perfectly, while it instantly loses a negative one; (2) that an uncharged electrode immersed in this gas acquires a positive charge.

If the spark length is increased until the discharge passes as a spark, then the electrode leaked slowly, whether charged positively or negatively; the leak in this case is, however, very small compared to that which exists when the discharge passes as an arc.

Hydrogen.

When similar experiments are tried in hydrogen, the results are quite different.

When the *arc* discharge passes through hydrogen the electrode E always leaks when it is charged positively; it does not merely lose its positive charge, but acquires a negative one, its potential falling to U, where U is a quantity that depends on the size of the arc, and on its proximity to the electrode; in my experiments 5 or 6 volts was a common value for U. If the electrode E is initially uncharged, it acquires a negative charge, the potential falling to U, while if it is initially charged negatively it leaks if the negative potential is greater than U, until the negative potential falls to U, when no further leak occurs; if the negative potential is less than U, the negative charge on the electrode increases until the potential becomes equal to U, when it remains steady.

It is much more difficult to get a good arc in hydrogen than in oxygen, and, as it is essential to the success of the preceding experiments that the discharge should pass as a well-developed arc, the experiments with hydrogen are a little more troublesome than those with oxygen.

These experiments show that the oxygen in or near the arc discharges a negatively electrified body, but not a positively electrified one, while the hydrogen in or near the arc discharges a positively electrified body, but not a negatively electrified one. And also that an unchanged electrode becomes positively electrified in the oxygen, negatively electrified in the hydrogen.

I next endeavoured to see if this charging up of the electrodes is due to an electrification developed by the contact of the gas in the arc with the electrode, or whether this gas behaved as if it possessed an independent charge of electricity.

If the electrification is due to the contact of the gas with the electrode, then it ought to disappear when the electrode is covered with a layer of a non-conductor; if, however, the gas in the arc behaves as if it were charged, then, even though the electrode is covered with a non-conductor, the electrostatic induction due to the charge on the gas ought to produce a deflection of the electrometer in the same direction as if the electrode were uncovered.

I tried, therefore, the effect of covering the electrode with glass, with mica, with ebonite, and sulphur. I found that, in all these cases, the electrometer was deflected as long as the arc existed, and that the deflection was in the direction corresponding to a positive charge when the arc was in oxygen, and in that corresponding to a negative one when the arc was in hydrogen. The deflection, though not so large as when the electrode was bare, was quite unmistakable. It disappeared almost entirely as soon as the arc stopped.

Another experiment which I tried was to surround the arc by a large glass tube, coated inside and out with a thin layer of sulphur to prevent conduction over its surface. A ring of tin-foil was placed outside the tube, so as to surround the place where the arc passed; this ring was connected with one of the quadrants of an electrometer. As a further precaution against the creeping of the electricity over the surface of the tube, two thin rings of tin-foil, connected to the earth, were placed round the ends of the tube. In this case, when the arc passed through oxygen the quadrants of the electrometer connected with the central ring of tin-foil were *positively* charged by induction, while when the arc passed through hydrogen these quadrants were negatively charged. These experiments show that the oxygen in the arc behaves as if it had a charge of positive electricity, while the hydrogen in the arc behaves as if it had a charge of negative electricity.

The electrodes in the preceding experiments were so large that they were not heated sufficiently by the arc discharge to become luminous.

Elster and Geitel found that a metal plate placed near a red-hot platinum wire became positively electrified if the plate and the wire were surrounded by oxygen, negatively electrified if they were surrounded by hydrogen. If we suppose that the effect of the hot wire is to make the surrounding gas in a condition resembling the gas in the arc, Elster and Geitel's results would be explained by the preceding experiments, for these have shown that when this gas is oxygen it is positively electrified, and when hydrogen negatively electrified.

The following explanation of the results of the experiments on the electrolysis of steam seems to be that which agrees best with the preceding investigation.

When an electric discharge passes through a gas the properties of the gas in the neighbourhood of the line of discharge are modified. Thus, as Hittorf and Schuster have shown, the gas in the neighbourhood of the discharge is no longer an insulator, but can transmit a current under a very small potential difference. Faraday's remark, that when once a spark has passed through a gas the passage of another following it immediately afterwards is very much facilitated, is another example of the same thing. We have thus good reasons

for believing that when a spark passes through a gas it produces a supply of a modification of the gas, whose conductivity is enormously greater than that of the original gas. I have shown ('Phil. Mag.,' November, 1891) that the conductivity of this modified gas is comparable with that of strong solutions of electrolytes. When the discharge stops this modified gas goes back to its original condition. If now the discharges through the gas follow each other so rapidly that the modified gas produced by one discharge has not time to return to its original condition before the next discharge passes, the successive discharges will pass through this modified gas. If, on the other hand, the gas has time to revert to its original condition before the next discharge passes, then the discharges pass through the unmodified gas; we regard this as being accomplished by means of successive decompositions and recombinations of its molecules, analogous to those which, on Grotthus' theory of electrolysis, occur when a current passes through an electrolyte.

We regard the arc discharge as corresponding to the first of the preceding cases where the discharge passes through the modified gas, the spark discharge corresponding to the second when the discharge goes through the gas in its unmodified condition.

From this point of view, the explanation of the results of the experiments on the electrolysis of steam are very simple. The modified gas produced by the passage of the discharge through the steam consists of a mixture of hydrogen and oxygen, these gases being in the same condition as when the arc discharge passes through hydrogen and oxygen respectively, when, as we have seen, the hydrogen behaves as if it had a negative charge, the oxygen as if it had a positive one. Thus, in the case of the arc in steam, the oxygen, since it behaves as if it had a positive charge, will go to the negative, while the hydrogen, behaving as if it had a negative charge, will go to the positive electrode. We saw that this separation of the hydrogen and oxygen took place.

The correspondence between the quantities of hydrogen and oxygen from the electrolysis of the steam and those liberated by the electrolysis of water shows that the charges on the atoms of the modified oxygen and hydrogen are the same in amount, but opposite in sign to those we ascribe to them in ordinary electrolytes.

In the case of the long sparks where the discharge goes through the steam, since the molecule of steam consists of two positively charged hydrogen atoms and one negatively charged oxygen one, when the molecule splits up in the electric field the hydrogen will go towards the negative, the oxygen towards the positive, electrode, as in ordinary electrolysis. We saw (p. 103) that for long sparks through steam the hydrogen appeared at the negative, the oxygen at the positive, electrode.

I have much pleasure in thanking Mr. E. Everett for the assistance he has given me in the course of the preceding investigation.

III. "On the Geometrical Construction of the Oxygen Absorption Lines Great A, Great B, and α of the Solar Spectrum." By GEORGE HIGGS. Communicated by R. T. GLAZEBROOK, F.R.S. Received February 20, 1893.

[Publication deferred.]

IV. "Upon the Existence of more than one Fungus in Madura Disease (Mycetoma)." By RUBERT BOYCE, M.B., M.R.C.S., Assistant Professor of Pathology, University College, London, and NUSSERWANGI FAKIRGI SURVEYOR, M.D., M.R.C.P. Communicated by Professor VICTOR HORSLEY, F.R.S. Received February 21, 1893.

(From the Pathological Laboratory, University College, London.)

(Abstract.)

Nature of Mycetoma.—A very chronic, locally spreading inflammation of the foot, much less commonly of the hand; characterised by the destruction of the tissues, great overgrowth of granulation tissue, and by the presence of very numerous *brown-white*, fish-roe-like particles, or more rarely of *black* particles.

Views held concerning Mycetoma.—In 1874, Carter held that the "fungus foot" was a veritable parasitic disease, due to the growth and extension, within the tissues, of an "indigenous mould." He came to the conclusion that it was one species, the *Chionyphe Carteri*. Lewis and Cunningham (1888) concluded that mycetoma was "essentially a degeneration of the fatty tissues, independent of the local presence or influence of any parasites whatever." Bassini (1888) met with a case in Italy, the only one, as yet, observed in Europe, and concluded that the parasite was allied to the higher Fungi, either the Aspergilli or Mucorini. Most recently, Dr. Kanthack brought forward evidence to show the identity or close affinity of the parasite with that of actinomycosis.

Our Views.—That the black particles represent a curious metamorphosis of a large, branching, septate fungus; whilst the white particles consist largely of caseous material and of the remains of a lowly organised fungus, presenting in very many instances some of the characteristics of the fungus of actinomycosis. That both fungi are pathogenic. The following observations in support of these views are based upon an

FIG. 1.†

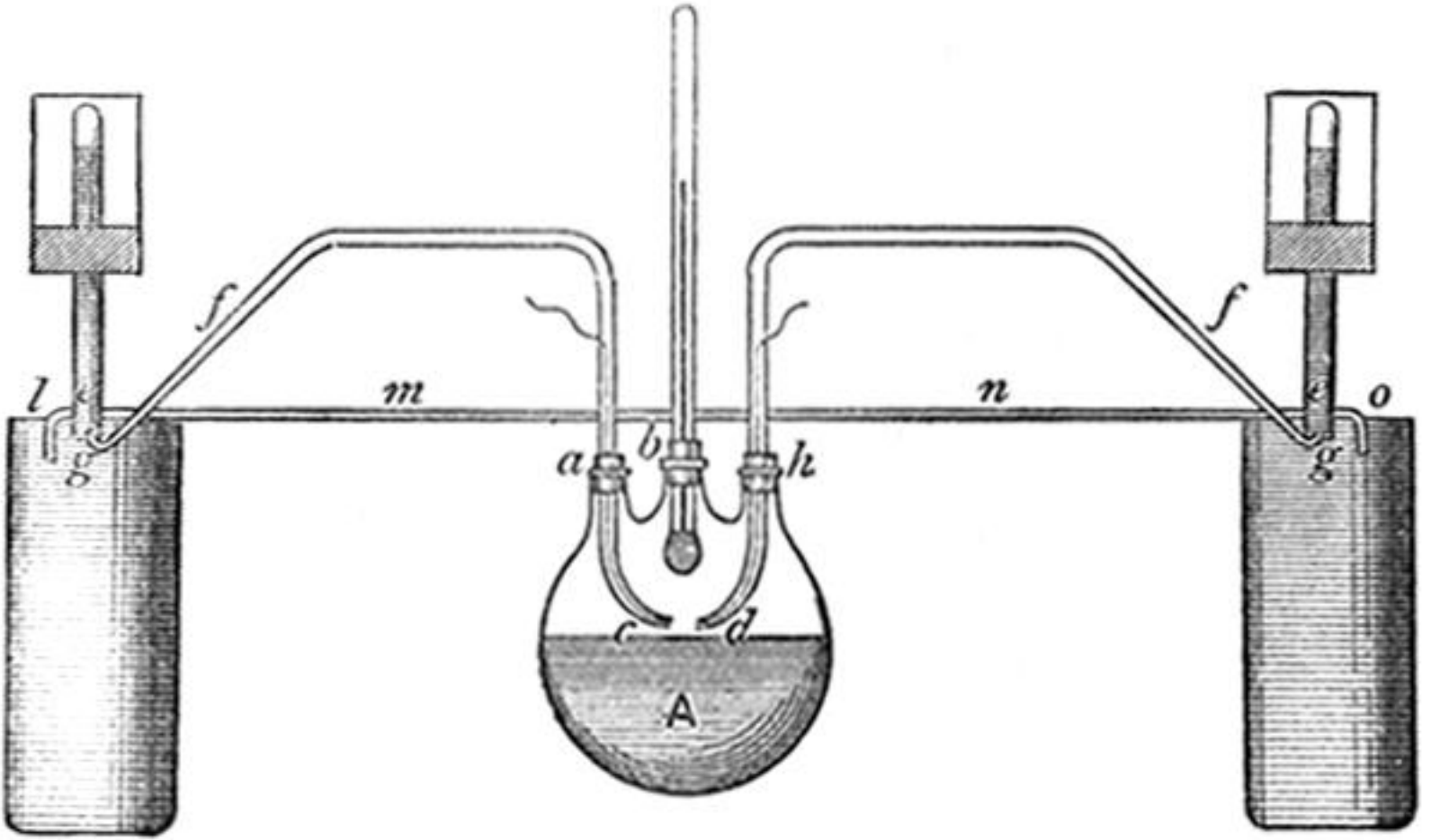


FIG. 3.

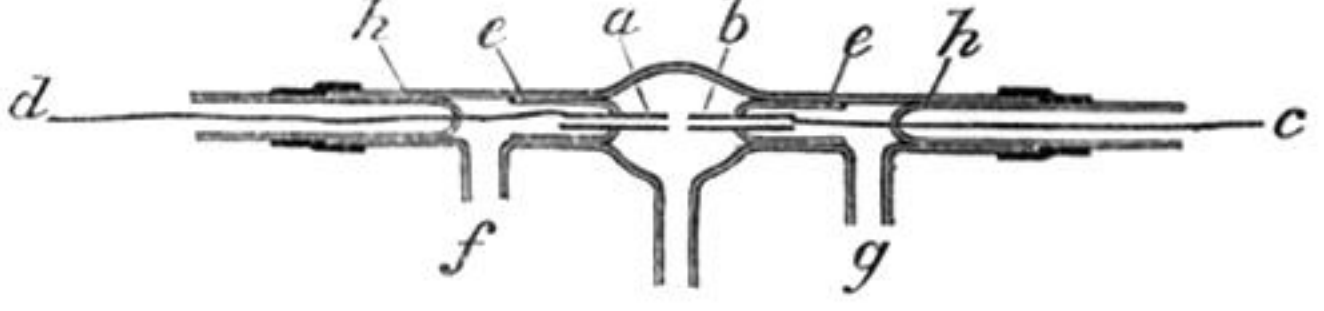


FIG. 5.