

$$\sqrt{\{2(E-V)\}} d\sigma \int_0^\pi N d\theta \cos^2 \theta, \quad \text{and} \quad \sqrt{\{2(E-V)\}} d\sigma \int_0^\pi N d\theta \sin^2 \theta$$

..... (8),

where $N d\theta$ denotes the number of portions of the path, per unit distance in the direction inclined $\frac{1}{2}\pi + \theta$ to x , which pass eitherwards across the area in directions inclined to x at angles between the values $\theta - \frac{1}{2}d\theta$ and $\theta + \frac{1}{2}d\theta$. The most general possible expression for N is, according to Fourier,

$$N = A_0 + A_1 \cos 2\theta + A_2 \cos 4\theta + \&c. \left. \begin{array}{l} \\ + B_1 \sin 2\theta + B_2 \sin 4\theta + \&c. \end{array} \right\} \dots\dots\dots (9).$$

Hence the two members of (8) become respectively

$$\sqrt{\{2(E-V)\}} d\sigma \frac{1}{2}\pi (A_0 + \frac{1}{2}A_1), \quad \text{and} \quad \sqrt{\{2(E-V)\}} d\sigma \frac{1}{2}\pi (A_0 - \frac{1}{2}A_1)$$

..... (10).

Remarking that A_0 and A_1 are functions of x , y , and taking $d\sigma = dx dy$, we find, from (10), for the two totals of (7) respectively

$$\left. \begin{array}{l} \frac{1}{2}\pi \iint dx dy (A_0 + \frac{1}{2}A_1) \sqrt{\{2(E-V)\}} \\ \text{and} \quad \frac{1}{2}\pi \iint dx dy (A_0 - \frac{1}{2}A_1) \sqrt{\{2(E-V)\}} \end{array} \right\} \dots\dots\dots (11),$$

where $\iint dx dy$ denotes integration over the whole space enclosed by (3). These quantities are equal if and only if $\iint dx dy A_1$ vanishes; it does so, clearly, if $\alpha = \beta$; but it seems improbable that, except when $\alpha = \beta$, it can vanish generally; and unless it does so, our present test case would disprove the Boltzmann-Maxwell general doctrine.

II. "On Electrical Evaporation." By WILLIAM CROOKES, F.R.S. Received June 4, 1891.

It is well known that when a vacuum tube is furnished with internal platinum electrodes, the adjacent glass, especially near the negative pole, speedily becomes blackened, owing to the deposition of metallic platinum. The passage of the induction current greatly stimulates the motion of the residual gaseous molecules; those condensed upon and in the immediate neighbourhood of the negative pole are shot away at an immense speed in almost straight lines, the speed varying with the degree of exhaustion and with the intensity of the induced current. Platinum being used for the negative pole,

not only are the gaseous molecules shot away from the electrode, but the passage of the current so affects the normal molecular motions of the metal as to remove some of the molecules from the sphere of attraction of the mass, causing them to fly off with the stream of gaseous molecules proceeding from the negative pole, and to adhere to any object near it. This property was, I believe, first pointed out by Dr. Wright, of Yale College, and some interesting experiments are described by him in 'The American Journal of Science and Arts.*' The process has been much used for the production of small mirrors for physical apparatus.

This electrical volatilisation or evaporation is very similar to ordinary evaporation by the agency of heat. Cohesion in solids varies according to physical and chemical constitution; thus every kind of solid matter requires to be raised to a certain temperature before the molecules lose their fixity of position and are rendered liquid, a result which is reached at widely different temperatures. If we consider a liquid at atmospheric pressure,—say, for instance, a basin of water in an open room,—at molecular distances the boundary surface between the liquid and the superincumbent gas will not be a plane, but turbulent like a stormy ocean. The molecules at the surface of the liquid dart to and fro, rebound from their neighbours, and fly off in every direction. Their initial velocity may be either accelerated or retarded according to the direction of impact. The result of a collision may drive a molecule in such a direction that it remains part and parcel of the liquid; on the other hand, it may be sent upwards without any diminution of speed, and it will then be carried beyond the range of attraction of neighbouring molecules and fly off into and mingle with the superincumbent gas. If a molecule of the liquid has been driven at an angle with a velocity not sufficient to carry it beyond the range of the molecular attraction of the liquid it may still escape, since, in its excursion upwards, a gaseous molecule may strike it in the right direction, and its temporary visit may be converted into permanent residence.

The intrinsic velocity of the molecules is intensified by heat and diminished by cold. If, therefore, we raise the temperature of the water without materially increasing that of the surrounding air, the excursions of the molecules of the liquid are rendered longer and the force of impact greater, and thus the escape of molecules into the upper region of gas is increased, and we say that evaporation is augmented.

If the initial velocities of the liquid molecules can be increased by any other means than by raising the temperature, so that their escape into the gas is rendered more rapid, the result may be called "evaporation" just as well as if heat had been applied.

* Third Series, vol. 12, p. 49, January, 1877, and vol. 14, p. 169, September, 1877.

Hitherto I have spoken of a liquid evaporating into a gas; but the same reasoning applies equally to a solid body. But whilst a solid body like platinum requires an intense heat to enable its upper stratum of molecules to pass beyond the sphere of attraction of the neighbouring molecules, experiment shows that a very moderate amount of negative electrification superadds sufficient energy to enable the upper stratum of metallic molecules to fly beyond the attractive power of the rest of the metal.

If a gaseous medium exists above the liquid or solid, it prevents to some degree the molecules from flying off. Thus both ordinary and electrical evaporation are more rapid in a vacuum than at the ordinary atmospheric pressure.

I have recently made some experiments upon the evaporation of different substances under the electric stress.

Evaporation of Water.—A delicate balance was taken, and two very shallow porcelain dishes were filled with acidulated water and balanced on the pans. Dipping into each dish—touching the liquid, but not the dish—was a platinum wire, one connected with the induction coil and the other insulated. The balance was left free to move, but was not swinging, the pointer resting at the centre of the scale. The water in connection with the coil was first made positive. After $1\frac{3}{4}$ hours there was scarcely any difference between the weight of the insulated water and that which had been exposed to the positive current. Equilibrium being restored, the current was reversed, the negative current being kept on the dish for two hours. At the end of this time the electrified water was decidedly lighter. After having again restored equilibrium, the electrification of the dishes was reversed, *i.e.*, the one that had before been insulated was made negative and the other one was insulated. In an hour the electrified water had become decidedly lighter than the insulated water. The experiment was performed in a room of uniform temperature, and any draught was prevented by the glass case of the balance. In a subsequent experiment in which the quantities were weighed, it was found that negatively electrified water lost in $1\frac{1}{2}$ hours $1/1000$ th part of its weight more than did insulated water.

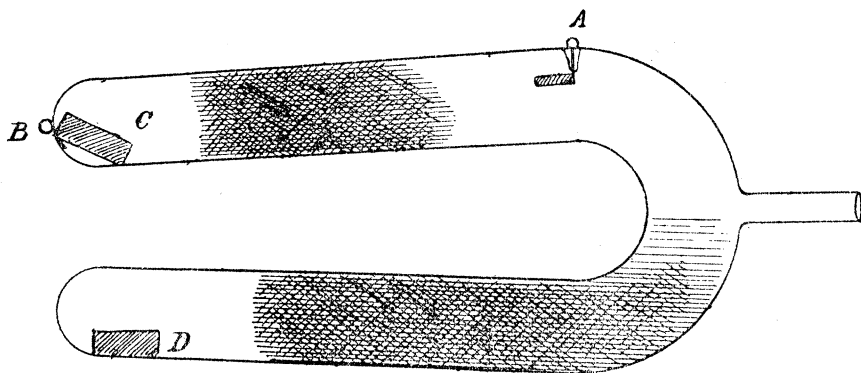
This experiment shows that the disturbing influence which assists evaporation is peculiar to the negative pole even at atmospheric pressures.

The metal cadmium was next experimented upon.

Evaporation of Cadmium.—If the flying-off of the metal of the negative pole is similar to evaporation or volatilisation, the operation should be accelerated by heat.

A tube was made as shown in fig. 1. A and B are the platinum poles sealed through the glass. C and D are two blocks of metallic cadmium of the same size and weight. The piece C is in contact

FIG. 1.



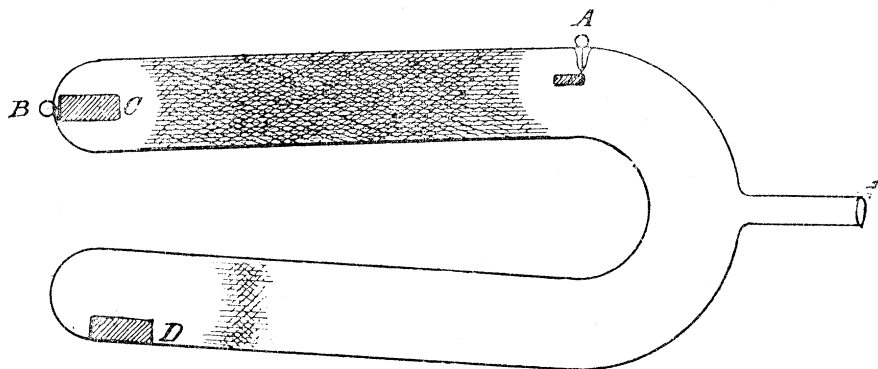
with the pole B, which in the experiment was always kept negative, the pole A being positive. When the exhaustion was such that the passage of the current gave green phosphorescence over the glass, heat was applied simultaneously to both ends of the U-shaped tube by means of a gas-burner and air-bath, so that one piece of cadmium was at the same temperature as the other. The current was then applied and was kept on for about an hour, and it was remarkable that no metal was deposited in the neighbourhood of the positive pole, the surrounding portion of the tube being quite clean, while the corresponding part of the other limb of the tube, having no electrodes, was thickly coated, the appearance being shown in the drawing.

As the temperature was high, metal had distilled off from both lumps; hence there was no visible difference in the amount of the deposit in the two sides. It is evident that, to render the electrical action most visible, the temperature should be kept short of the normal volatilising point.

In the next experiment an exactly similar tube was used; the vacuum was such that the green phosphorescence of the glass was well seen, the temperature was kept just below the melting point of cadmium, and the current was kept on for an hour. On examining the tube at the end of this time, the appearance was as seen in fig. 2. A considerable deposit had taken place on the end of the tube near the negative pole, the space round the positive pole was clear, while in the limb of the tube where no electricity had been passing only a very little deposit of metal was seen, as shown in the figure.

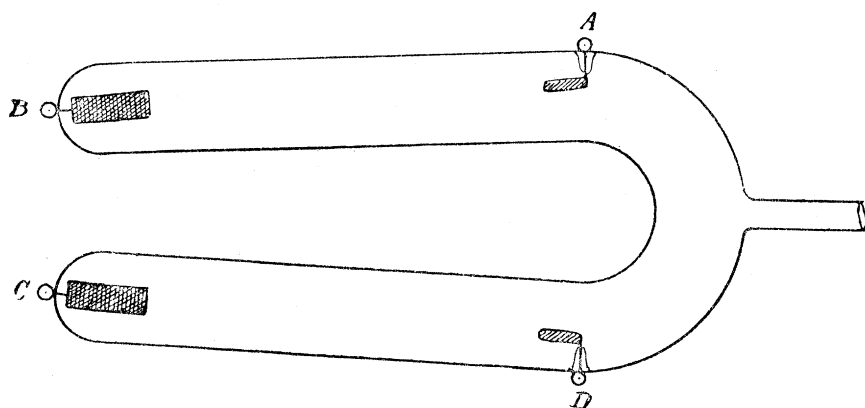
The temperature in this experiment having been kept below the melting point, had no electricity been applied, there would have been very little, if any, evaporation. The amplitude of the molecular oscillations was increased by the rise of temperature, but not suffi-

FIG. 2.



ciently to allow many of the molecules to pass beyond the sphere of attraction of the mass. When, however, the current was turned on, the oscillations were increased sufficiently to carry some of the molecules beyond their spheres of attraction and hence into the vacuous space above. As in the water experiment, this only happens at the negative pole. It would seem that, even after having been *removed* from the rest of the mass, the on-rushing stream of gaseous molecules is necessary to carry the metallic molecules away, and, as I shall presently show, even then they very quickly drop out of the ranks and deposit on the walls of the tube.

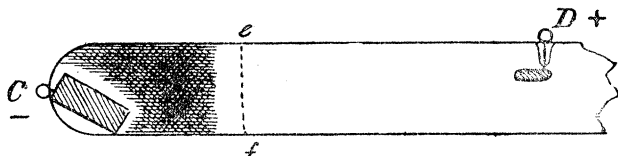
FIG. 3.



Another tube was made as shown in fig. 3. The poles A, B, C, D were platinum wires sealed through the glass, A and D having aluminium poles covering the platinum wire. In the ends of the

tube, and touching the poles B and C, were two pieces of cadmium of the same size and shape. The tube was exhausted to the phosphorescent point, and the current was turned on, C being made negative and D positive. No heat was applied. The current was kept on for about half an hour, until a good deposit of metal had been deposited on the glass, the appearance being as shown in fig. 4,

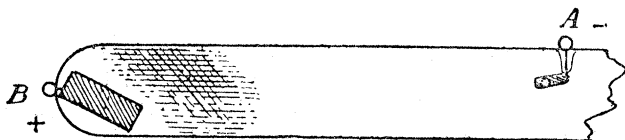
FIG. 4.



the glass near the pole C being coated with metal, while the glass round the pole D was clean. The outer boundary of the dark space during the experiment is shown by the dotted line *ef*.

The pole B was now made positive and the pole A negative, the current being kept on for another half hour. At the end of the time the only additional effect was a slight darkening round the lump of cadmium, in the same place as, but very much fainter than, the deposit shown in fig. 5. This is probably due to a little leakage of negative

FIG. 5.

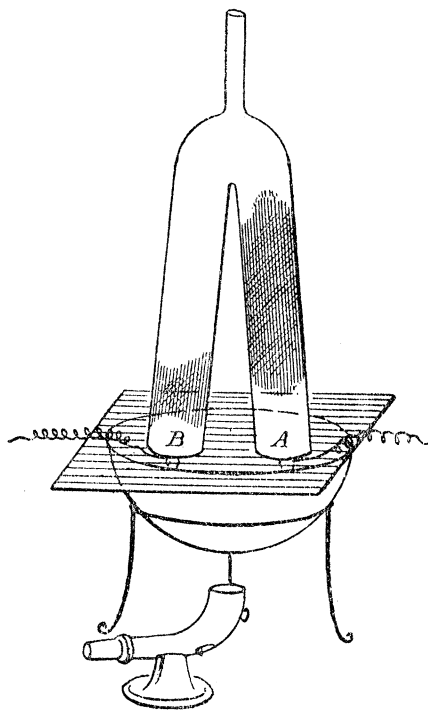


discharge from the positive pole. The experiment shows that positive electrification does not cause the metal sensibly to volatilise.

In these experiments no estimation was made of the weight of metal removed, and the cadmium only rested by its own weight upon the platinum wires that had been sealed through the glass. To render the experiment quantitative, and at the same time to remove any disturbing effect that might be caused by heating at the point of indifferent contact, the following experiments were made:—

A U-shaped tube, shown in fig. 6, had a platinum pole sealed in each end. 6 grains of pure cadmium were put into each limb and fused round the platinum wire. The ends of the tube were then put into an air-bath, and kept at a temperature of 200° C. during the

FIG. 6.

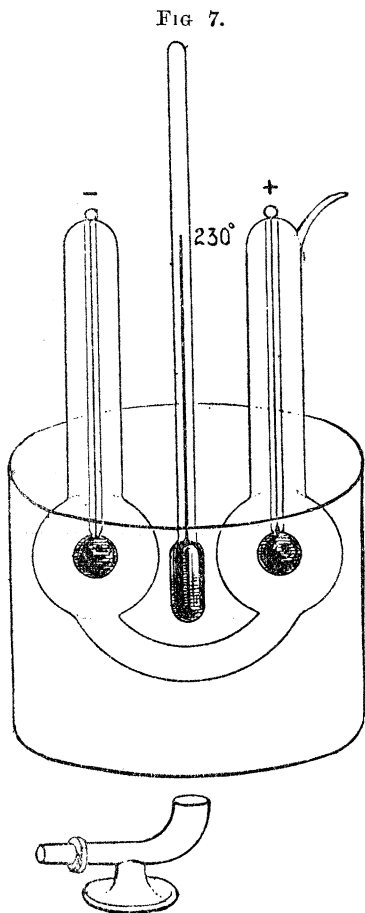


continuance of the experiment.* The exhaustion remained at 0·00076 mm., or 1 M. The induction current was kept going for thirty-five minutes, the pole A being negative and B positive. At the end of this time it was seen that most of the cadmium had disappeared from the negative pole, leaving the platinum wire clean, no metal being deposited near it, and the molecules appearing to have been shot off to a distance of about $\frac{3}{4}$ inch. The appearance of the positive pole was very different; scarcely any of the cadmium had been volatilised, and the condensed metal came almost close to the pole. The tube was opened, and the remaining wires and metal were weighed. The cadmium was then dissolved off the poles in dilute acid; the residue was washed, dried, and weighed.

	Positive pole.	Negative pole.
Original weight of cadmium	6·00 grs.	6·00 grs.
Cadmium remaining on the pole . . .	3·65 „	0·25 „
Cadmium volatilised in 35 mins. . .	2·35 „	5·75 „

* Cadmium melts at 320° and boils at 860°.

The difference between the amount of cadmium driven from the two poles having proved to be so decided, another experiment was tried in a tube so arranged that the metal could be more easily weighed before and after the experiment. The apparatus is shown in fig. 7. A tube was blown U-shaped, having a bulb in each limb.



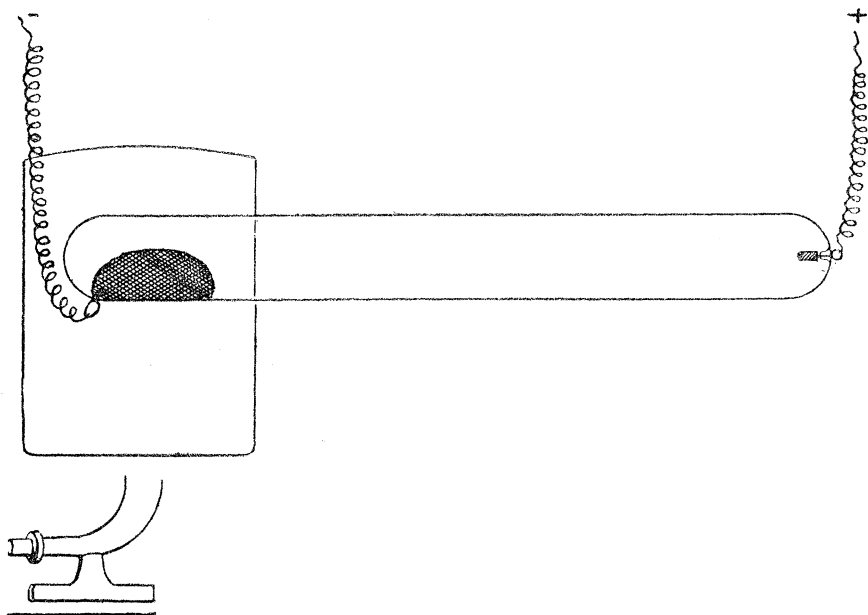
The platinum poles were, as before, at the extremities of each limb, and in each bulb was suspended from a small platinum hook a small lump of cadmium, the metal having been cast on to the wire. The wires were each weighed with and without the cadmium. The tube was exhausted, and the lower half of the tube was enclosed in a metal pot containing paraffin wax, the temperature being kept at 230° C.

during the continuance of the experiment. A deposit around the negative pole took place almost immediately, and in five minutes the bulb surrounding it was opaque with deposited metal. The positive pole with its surrounding luminosity could be easily seen the whole time. In thirty minutes the experiment was stopped, and after all was cold the tube was opened and the wires weighed again. The results were as follows:—

	Positive pole.	Negative pole.
Original weight of cadmium	9.34 grs.	9.38 grs.
Weight after experiment	9.25 „	1.86 „
Cadmium volatilised in 30 mins. ..	0.09 „	7.52 „

Finding that cadmium volatilised so readily under the action of the induction current, a large quantity, about 350 grs., of the pure metal, was sealed up in a tube arranged as in fig. 8, and the end of

FIG. 8.



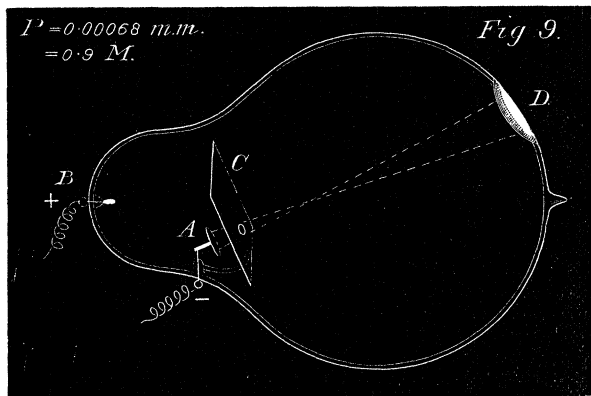
the tube containing the metal was heated to a little above the melting point; the molten metal being made the negative pole, in a few hours the whole quantity had volatilised and condensed in a thick layer on the far end of the tube, near, but not touching, the positive pole.

Volatilisation of Silver.—Silver was the next metal experimented

upon. The apparatus was similar to that used for the cadmium experiments (fig. 7). Small lumps of pure silver were cast on the ends of platinum wires, and suspended to the inner ends of platinum terminals passing through the glass bulb. The platinum wires were protected by glass, so that only the silver balls were exposed. The whole apparatus was enclosed in a metal box lined with mica, and the temperature was kept as high as the glass would allow without softening. The apparatus was exhausted to a dark space of 3 mm., and the current was kept on for $1\frac{1}{2}$ hours. The weights of silver, before and after the experiment, were as follows:—

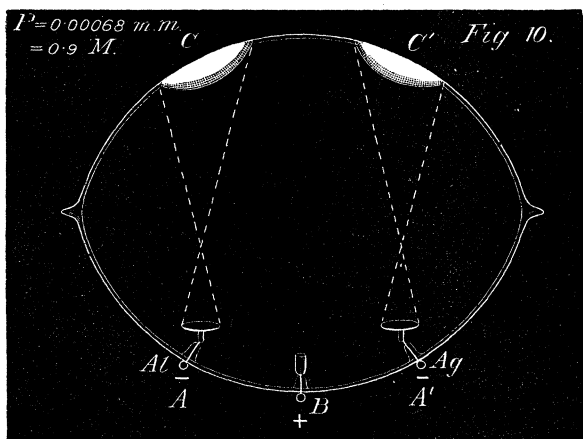
	Positive pole.	Negative pole.
Original weight of silver.....	18·14 grs.	24·63 grs.
Weight after the experiment....	18·13 „	24·44 „
Silver volatilised in $1\frac{1}{2}$ hours	0·01 „	0·19 „

It having been found that silver volatilised readily from the negative pole in a good vacuum, experiments were instituted to ascertain whether the molecules of metal shot off from the pole were instrumental in producing phosphorescence. A glass apparatus was made as shown in fig. 9. A pear-shaped bulb of German glass



has, near the small end, an inner concave negative pole, A, of pure silver, so mounted that its inverted image is thrown upon the opposite end of the tube. In front of the pole is a screen of mica, having a small hole in the centre, so that only a narrow pencil of rays from the silver pole can pass through, forming a bright spot of phosphorescence, D, at the far end of the bulb. The exhaustion was pushed to a high point, 0·00068 mm., or 0·9 M. The current from an induction coil was allowed to pass continuously for some hours, the silver

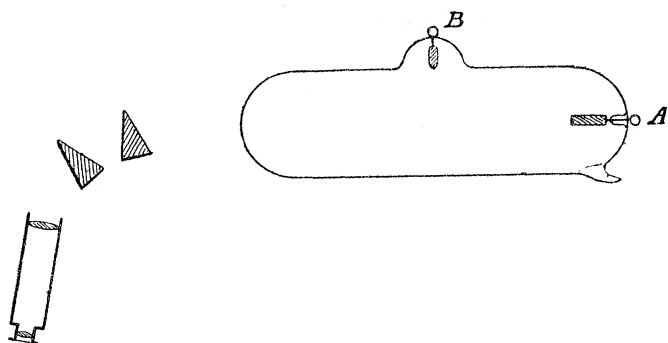
pole being kept negative, so as to drive off a certain portion of the silver electrode. On subsequent examination it was found that the silver had all been deposited in the immediate neighbourhood of the pole, whilst at the far end of the tube the spot D, that had been continuously glowing with phosphorescent light, was practically free from silver.



A tube was next made as shown in fig. 10. It had two negative poles connected together, A, A', so placed as to project two luminous spots on the phosphorescent glass of the tube. One of the electrodes, A', was of silver, a volatile metal; the other, A, was of aluminium, practically non-volatile. On connecting the two negative poles, A, A', with one terminal of the coil, and the positive pole, B, with the other terminal, it was seen in the course of half an hour that a considerable quantity of metal had been projected from the silver negative pole, blackening the tube in its neighbourhood, while no projection of metallic particles took place from the aluminium positive pole. During the whole time of the experiment, however, the two patches of phosphorescent light, C and C', had been glowing with exactly the same intensity, showing that the active agent in effecting phosphorescence was not the molecules of the solid projected from the poles, but the residual gaseous particles, or "radiant matter."

In the tubes hitherto made containing silver, it had not been easy to observe the spectrum of the negative pole, owing to the rapid manner in which the deposit obscured the glass. A special tube (fig. 11) was therefore devised, of the following character. The silver pole, A, was attached to the platinum pole at one end of the tube, and the aluminium positive pole, B, was at the side. The end of the tube opposite the silver pole was rounded, and the spectroscope was

FIG. 11.



arranged to observe the light of the volatilising silver “end on,” as shown in the figure. In this way the deposit of silver offered no obstruction to the light, as none was deposited except on the sides of the tube surrounding the silver. At a vacuum giving a dark space of about 3 mm. from the silver, a greenish-white glow was seen to surround the metal. This glow gave a very brilliant spectrum. The spark from silver poles in air was brought into the same field of view as the vacuum glow, by means of a right-angled prism attached to the spectroscope, and the two spectra were compared. The two strong green lines of silver were visible in each spectrum; the measurements taken of their wave-lengths were 3344 and 3675, numbers which are so close to Thalén’s numbers as to leave no doubt that they are the silver lines. At a pressure giving a dark space of 2 mm. the spectrum was very bright, and consisted chiefly of the two green lines and the red and green hydrogen lines. The intercalation of a Leyden jar into the circuit does not materially increase the brilliancy of the lines, but it brings out the well-known air lines. At this pressure not much silver flies off from the pole. At a higher vacuum, the luminosity round the silver pole gets less and the green lines vanish. At an exhaustion of about one-millionth of an atmosphere the luminosity is feeble, the silver pole has exactly the appearance of being red hot, and the volatilisation of the metal proceeds rapidly.*

* Like the action producing volatilisation, the “red heat” is confined to the superficial layers of molecules only. The metal instantly assumes, or loses, the appearance of red heat the moment the current is turned on or off, showing that, if the appearance is really due to a rise of temperature, it does not penetrate much below the surface. The extra activity of the metallic molecules necessary to volatilise them is, in these experiments, confined to the surface only, or the whole mass would evaporate at once, as when a metallic wire is deflagrated by the discharge of a powerful Leyden jar. When this extra activity is produced by artificial heat one of the effects is the emission of red light; so it is not unreasonable

If, for the negative electrode, instead of a pure metal such as cadmium or silver, an alloy was used, the different components might be shot off to different distances, and in this way make an electrical separation—a sort of fractional distillation. A negative terminal was formed of clean brass, and submitted to the electrical discharge *in vacuo*; the deposit obtained was of the colour of brass throughout, and on treating the deposit chemically I could detect no separation of its component metals, copper and zinc.

[A remarkable alloy of gold and aluminium, of a rich purple colour, has been kindly sent me by Professor Roberts-Austen. Gold being very volatile in the vacuum tube, and aluminium almost fixed, this alloy was likely to give different results from those yielded by brass, where both constituents fly off with almost equal readiness. The AuAl alloy had been cast in a clay tube in the form of a rod 2 cm. long and about 2 mm. in diameter. It was sealed in a vacuum tube as the negative pole, an aluminium pole being at the other side. Part of the alloy, where it joined the platinum wire passing through the glass, was closely surrounded with a narrow glass tube; a clean glass plate was supported about 3 mm. from the rod of alloy. After good exhaustion the induction current was passed, the alloy being kept negative. Volatilisation was very slight, but at the end of half an hour a faint purple deposit was seen both on the glass plate and on the walls of the tube. On removing the rod from the apparatus, it was seen that the portion which had been covered by the small glass tube retained its original purple appearance, while the part that had been exposed to electrical action had changed to the dull white colour of aluminium. Examined under the microscope, the whitened surface of the Austen alloy was seen to be pitted irregularly, with no trace of crystalline appearance. This experiment shows that from an alloy of gold and aluminium the gold is the first to volatilise under electrical influence, the aluminium being left behind. The purple colour of the deposit on glass is probably due to finely divided metallic gold. The first deposit from a negative pole of pure gold is pink; this changes to purple as the thickness increases. The purple then turns to green, which gets darker and darker until the metallic lustre of polished gold appears.—June 10.]

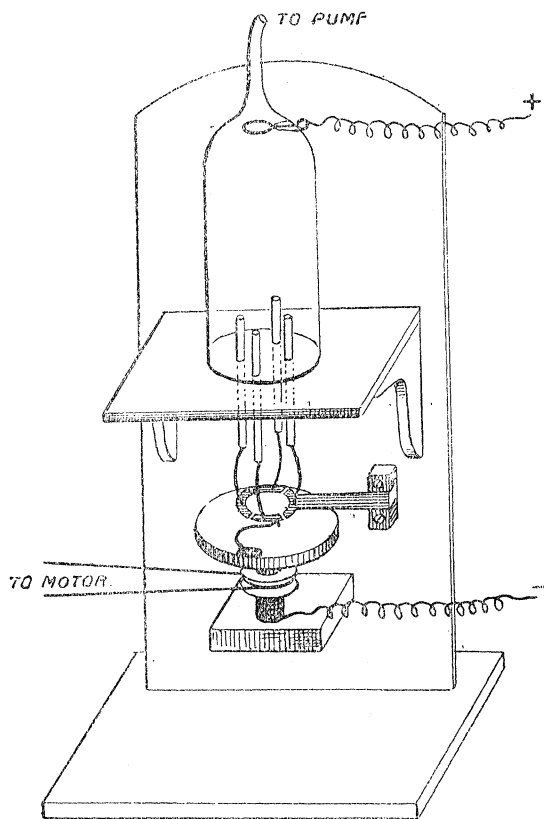
Returning to the analogy of liquid evaporation, if we take several liquids of different boiling points, put them under the same pressure, and apply the same amount of heat to each, the quantity passing

to imagine that when the extra activity is produced by electricity the emission of red light should also accompany the separation of molecules from the mass. In comparison with electricity heat is a wasteful agent for promoting volatilisation, as the whole mass must be raised to the requisite temperature to produce a surface action merely; whereas the action of electrification does not appear to penetrate much below the surface.

from the liquid to the gaseous state will differ widely in each case.

It was interesting to try a parallel experiment with metals, to find their comparative volatility under the same conditions of temperature, pressure, and electrical influence. It was necessary to fix upon one metal as a standard of comparison, and for this purpose I selected gold, its electrical volatility being great, and it being easy to prepare in a pure state.

FIG. 12.



An apparatus was made as in fig. 12. It is practically a vacuum tube with four negative poles at one end and one positive pole at the other. By a revolving commutator I was able to make electrical connection with each of the four negative poles in succession for exactly the same length of time (about six seconds); by this means

the variations in the strength of the current, the experiment lasting some hours, affected each metal alike.

The exposed surface of the various metals used as negative poles was kept uniform by taking them in the form of wires that had all been drawn through the same standard hole in the drawplate, and cutting them by gauge to a uniform length; the actual size used was 0·8 mm. in diameter, and 20 mm. long.

The comparison metal gold had to be used in each experiment; the apparatus thus enabled me to compare three different metals each time. The length of time that the current was kept on the revolving commutator in each experiment was eight hours, making two hours of electrification for each of the four negative electrodes; the pressure was such as to give a dark space of 6 mm.

The fusible metals, tin, cadmium, and lead, when put into the apparatus in the form of wires, very quickly melted. To avoid this difficulty a special form of pole was devised. Some small circular porcelain basins were made, 9 mm. diameter; through a small hole in the bottom a short length of iron wire, 0·8 mm. in diameter, was passed, projecting downwards about 5 mm.; the basin was then filled to the brim with the metal to be tested, and was fitted into the apparatus exactly in the same way as the wires; the internal diameter of the basins at the brim was 7 mm., and the negative metal filed flat was thus formed of a circular disc 7 mm. diameter. The standard gold pole being treated in the same way, the numbers obtained for the fusible metals can be compared with gold, and take their place in the table.

The following table of the comparative volatilities was in this way obtained, taking gold as = 100 :—

Palladium	108·00
Gold	100·00
Silver	82·68
Lead	75·04
Tin	56·96
Brass.....	51·58
Platinum	44·00
Copper	40·24
Cadmium	31·99
Nickel	10·99
Iridium.....	10·49
Iron	5·50

In this experiment equal surfaces of each metal were exposed to the current. By dividing the numbers so obtained by the specific gravity of the metal, the following order is found :—

Palladium.....	9.00
Silver	7.88
Tin	7.76
Lead	6.61
Gold	5.18
Cadmium.....	3.72
Copper	2.52
Platinum	2.02
Nickel	1.29
Iron	0.71
Iridium	0.47

Aluminium and magnesium appear to be practically non-volatile under these circumstances.

The order of metals in the table shows at once that the electrical volatility in the solid state does not correspond with the order of melting points, of atomic weights, or of any other well-known constant. The experiment with some of the typical metals was repeated, and the numbers obtained did not vary materially from those given above, showing that the order is not likely to be far wrong.

It is seen in the above table that the electrical volatility of silver is high, while that of cadmium is low. In the two earlier experiments, where cadmium and silver were taken, the cadmium negative electrode in 30 minutes lost 7.52 grs., whilst the silver negative electrode in $1\frac{1}{2}$ hours only lost 0.19 gr. This apparent discrepancy is easily explained by the fact (already noted in the case of cadmium) that the maximum evaporation effect, due to electrical disturbance, takes place when the metal is at or near the point of liquefaction. If it were possible to form a negative pole *in vacuo* of molten silver, then the quantity volatilised in a given time would be probably much more than that of cadmium.

Gold having proved to be readily volatile under the electric current, an experiment was tried with a view to producing a larger quantity of the volatilised metal. A tube was made having at one end a negative pole composed of a weighed brush of fine wires of pure gold, and an aluminium pole at the other end.

The tube was exhausted and the current from the induction coil put on, making the gold brush negative; the resistance of the tube was found to increase considerably as the walls became coated with metal, so much so that, to enable the current to pass through, air had to be let in after a while, depressing the gauge $\frac{1}{2}$ mm.

The weight of the brush before experiment was 35.4940 grs. The induction current was kept on the tube for $14\frac{1}{2}$ hours; at the end of this time the tube was opened and the brush removed. It now weighed 32.5613, showing a loss of 2.9327 grs. When heated

below redness the deposited film of gold was easily removed from the walls of the tube in the form of very brilliant foil.

After having been subjected to electrical volatilisation, the appearance of the residual piece of gold under the microscope, using a $\frac{1}{4}$ -inch object glass, was very like that of electrolytically deposited metal, pitted all over with minute hollows.

This experiment on the volatilisation of gold having produced good coherent films of that metal, a similar experiment was tried, using a brush of platinum as a negative electrode. On referring to the table it will be seen that the electrical volatility of platinum is much lower than that of gold, but it was thought that by taking longer time a sufficient quantity might be volatilised to enable it to be removed from the tube.

The vacuum tube was exhausted to such a point as to give a dark space of 6 mm., and it was found, as in the case of gold, that as a coating of metal was deposited upon the glass the resistance rapidly increased, but in a much more marked degree, the residual gas in the tube apparently becoming absorbed as the deposition proceeded. It was necessary to let a little air into the tube about every 30 minutes, to reduce the vacuum. This appears to show that the platinum was being deposited in a porous spongy form, with great power of occluding the residual gas.

Heating the tube when it had become in this way non-conducting liberated sufficient gas to depress the gauge of the pump 1 mm., and to reduce the vacuum so as to give a dark space of about 3 mm. This gas was not re-absorbed on cooling, but on passing the current for ten minutes the tube again refused to conduct, owing to absorption. The tube was again heated, with another liberation of gas, but much less than before, and this time the whole was re-absorbed on cooling.

The current was kept on this tube for 25 hours; it was then opened, but I could not remove the deposited metal except in small pieces, as it was brittle and porous. Weighing the brush that had formed the negative pole gave the following results:—

	Grains.
Weight of platinum before experiment.....	10·1940
„ after experiment	8·1570
Loss by volatilisation in 25 hours	2·0370

Another experiment was made similar to that with gold and platinum, but using silver as the negative pole, the pure metal being formed into a brush of fine wires. Less gas was occluded during the progress of this experiment than in the case of platinum. The silver behaved the same as gold, the metal deposited freely, and the vacuum was easily kept at a dark space of 6 mm. by the very occasional admis-

sion of a trace of air. In 20 hours nearly 3 grs. of silver were volatilised. The deposit of silver was detached without difficulty from the glass in the form of brilliant foil.

III. "A Study of the Planté Lead-Sulphuric Acid-Lead Peroxide Cell, from a Chemical Stand-point. Part I." By G. H. ROBERTSON. Communicated by Professor ARMSTRONG, F.R.S. Received May 27, 1891.

(Abstract.)

The author, in the introduction, states that though, since Frankland in 1883 published his first "Contribution to the Chemistry of Storage Batteries," the capabilities of the Planté cell have been well tested and are now thoroughly understood, there is still considerable uncertainty as to the precise nature of the chemical changes which attend their use; and that it was principally to study the part played by the electrolyte that the investigation, the results of which are recorded in this paper, was instituted about a year ago at the Central Institution at Dr. Armstrong's suggestion, as McLeod's observations on the electrolysis of sulphuric acid solutions led to the supposition that the changes occurring in the acid were probably less simple than was commonly supposed. This supposition was verified.

The first section of the paper deals with the nature of the lead salt formed during discharge. It is pointed out that, as is well known, red lead varies considerably in composition, generally containing a smaller proportion of peroxide than is represented by the formula $Pb_3O_4 = PbO_2 \cdot 2PbO$; and that with nitric acid it behaves as though it were a mixture of the two oxides, the nitric acid always dissolving out the monoxide. There is no reason why sulphuric acid should not behave similarly, and, since lead sulphate is but very slightly soluble, red lead may be expected always to yield a corresponding sulphate, *i.e.*, a mixture of peroxide and sulphate, containing an amount of sulphate corresponding to the amount of monoxide originally present in combination with the peroxide. At Dr. Armstrong's request a number of experiments were made at the Central Institution (long prior to the reading of Messrs. Gladstone and Hibbert's papers) by two students, Messrs. Briggs and Ingold, on various samples of red lead, with the result that the sulphate formed always corresponded to the monoxide originally present.

As no proof of the existence of a definite homogeneous sulphate corresponding to red lead can be afforded by analysis alone, evidence must be obtained that the product differs in some of its properties from a mixture.

FIG. 1.

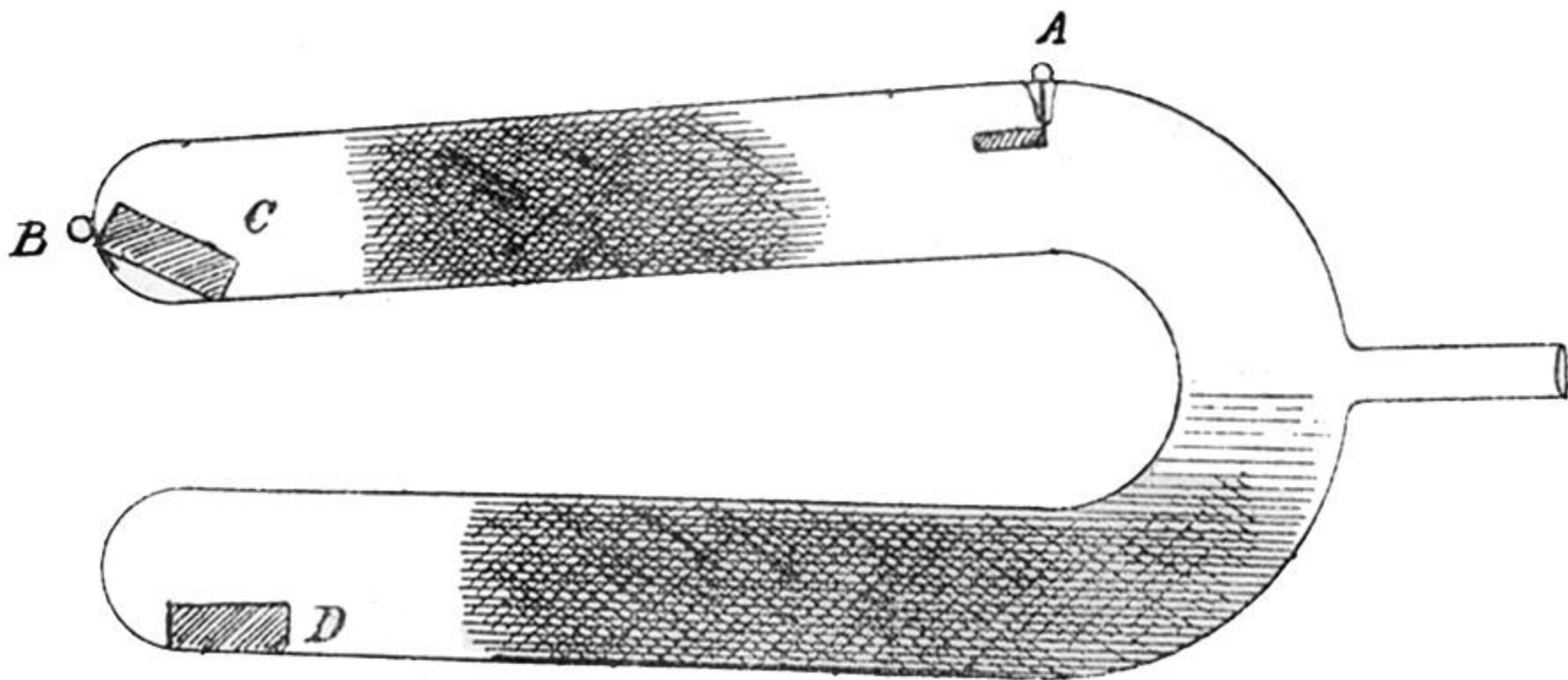


FIG. 2.

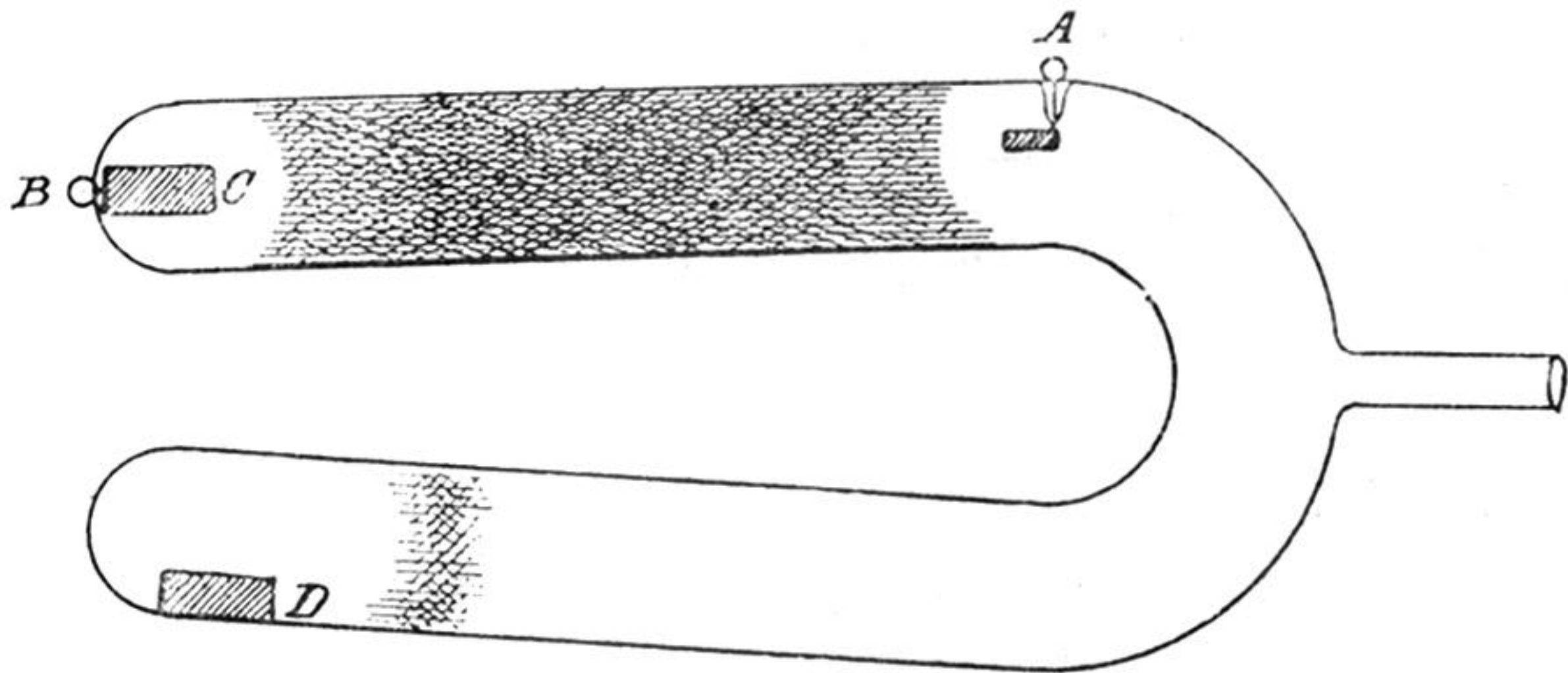


FIG. 3.

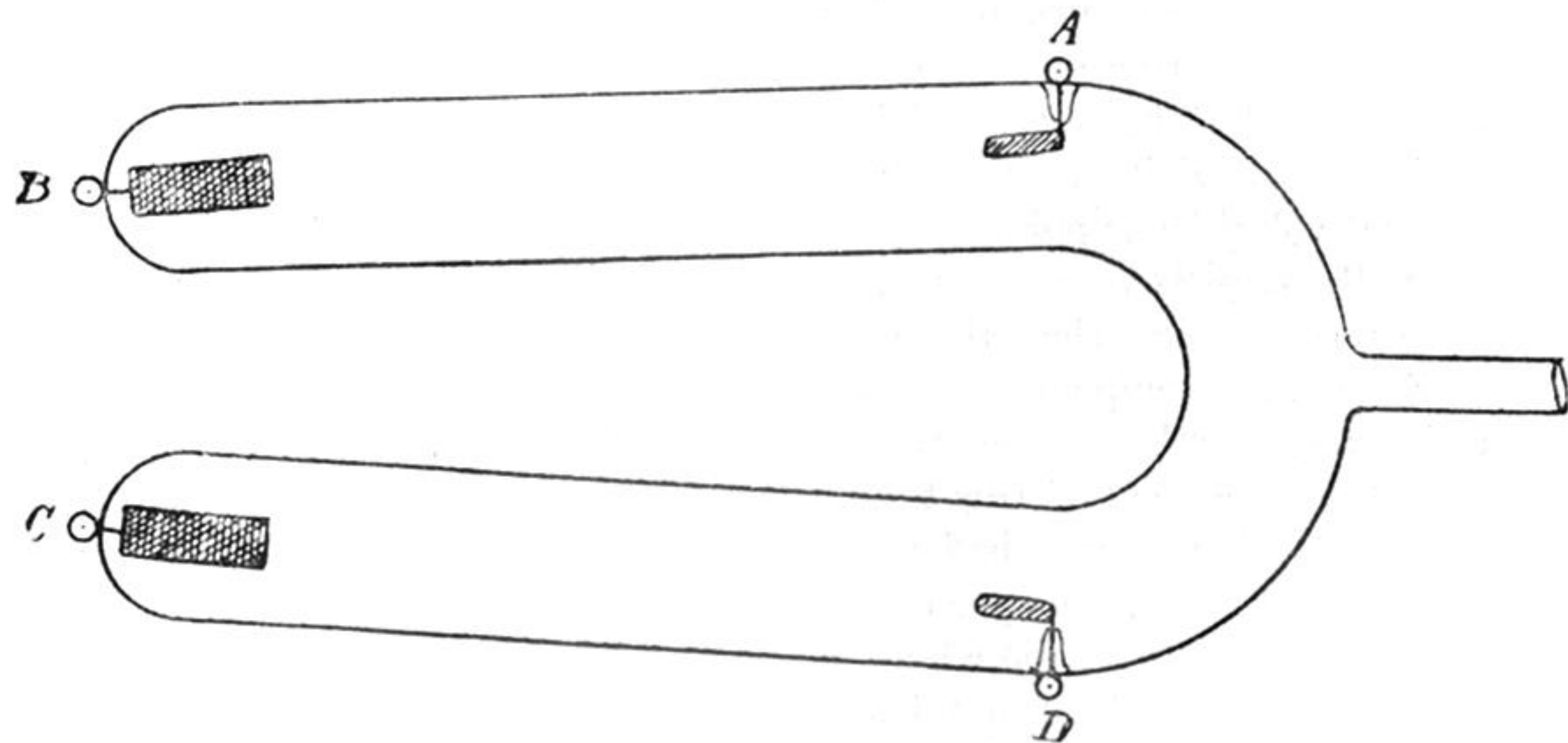


FIG. 4.

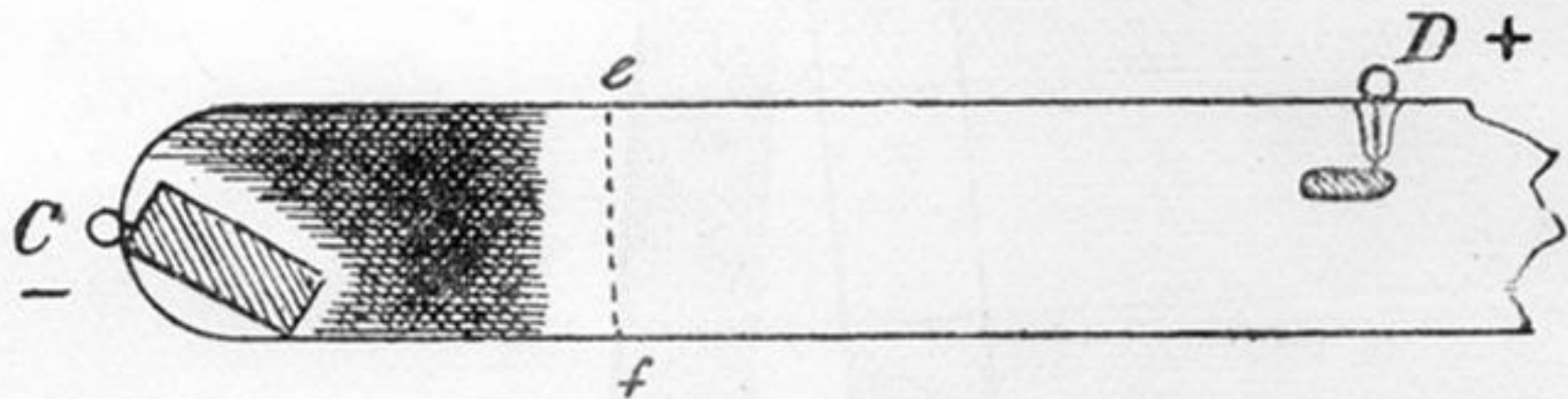


FIG. 5.

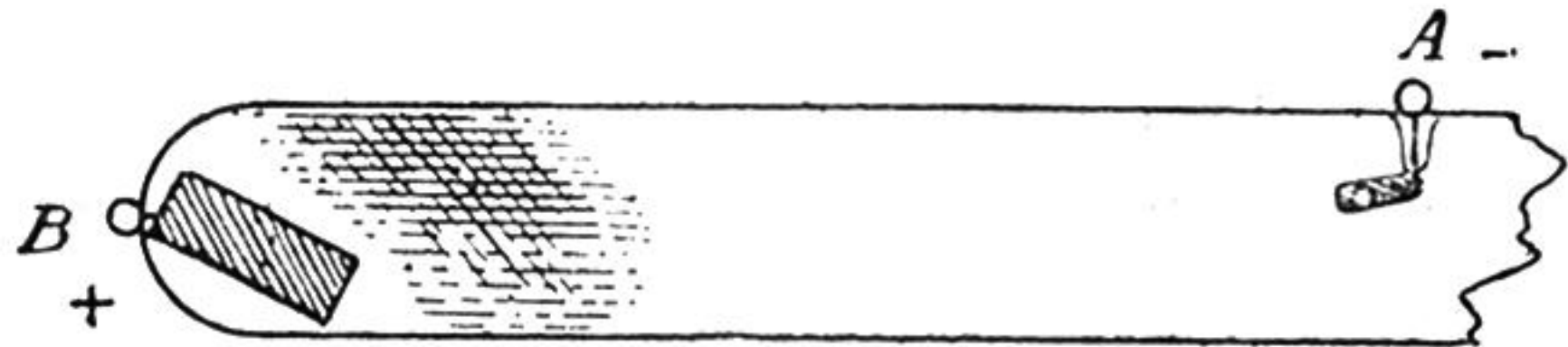


FIG. 6.

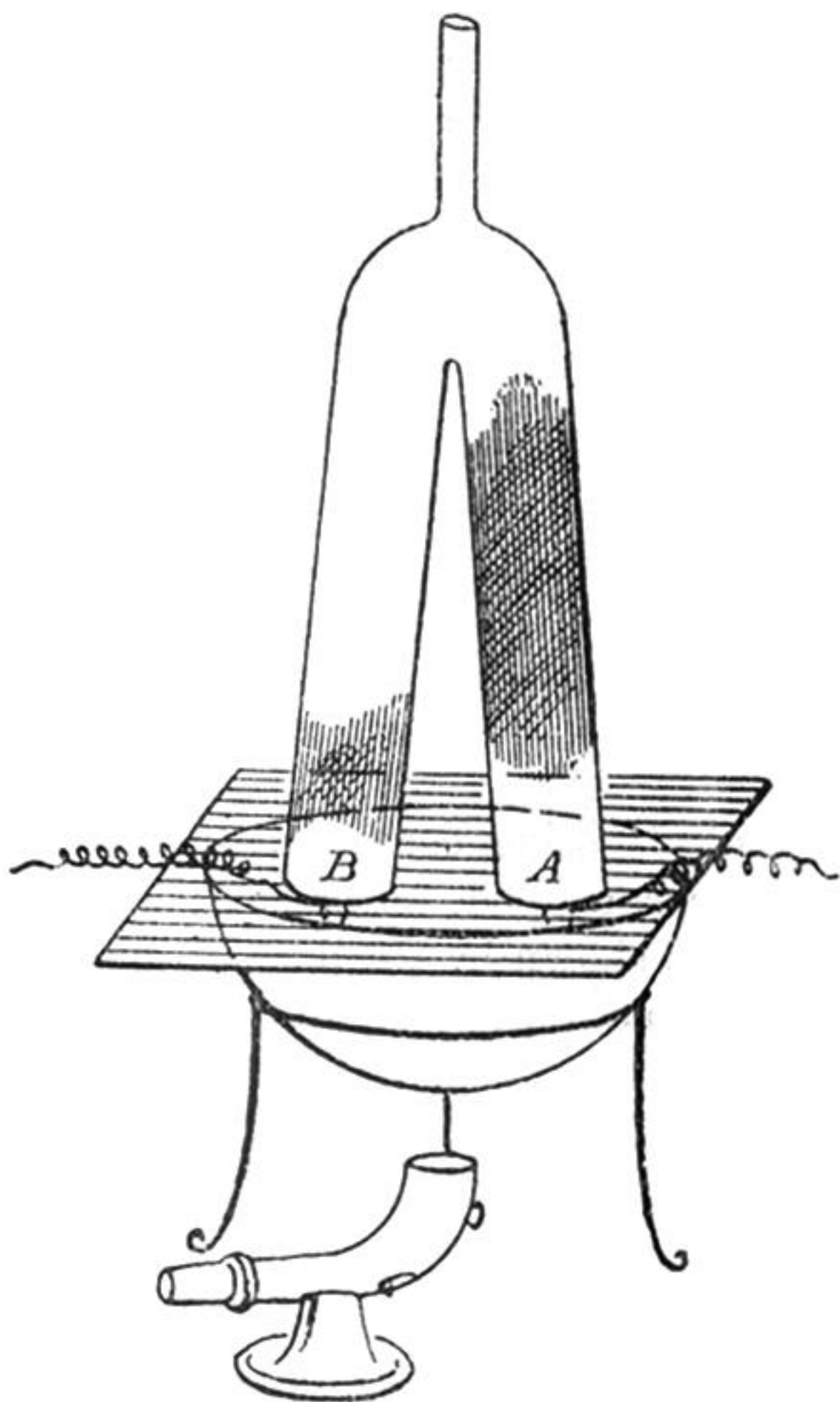
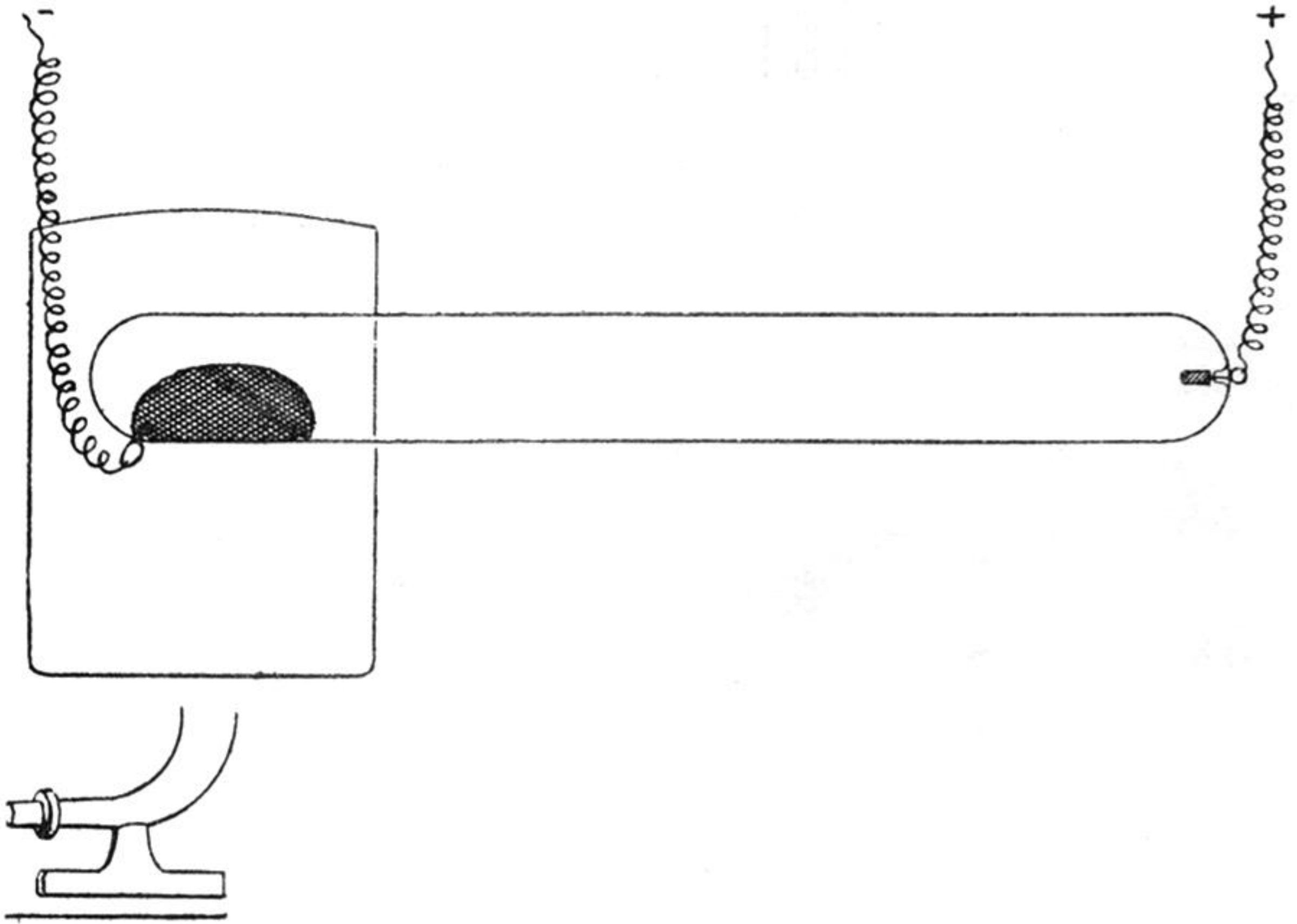
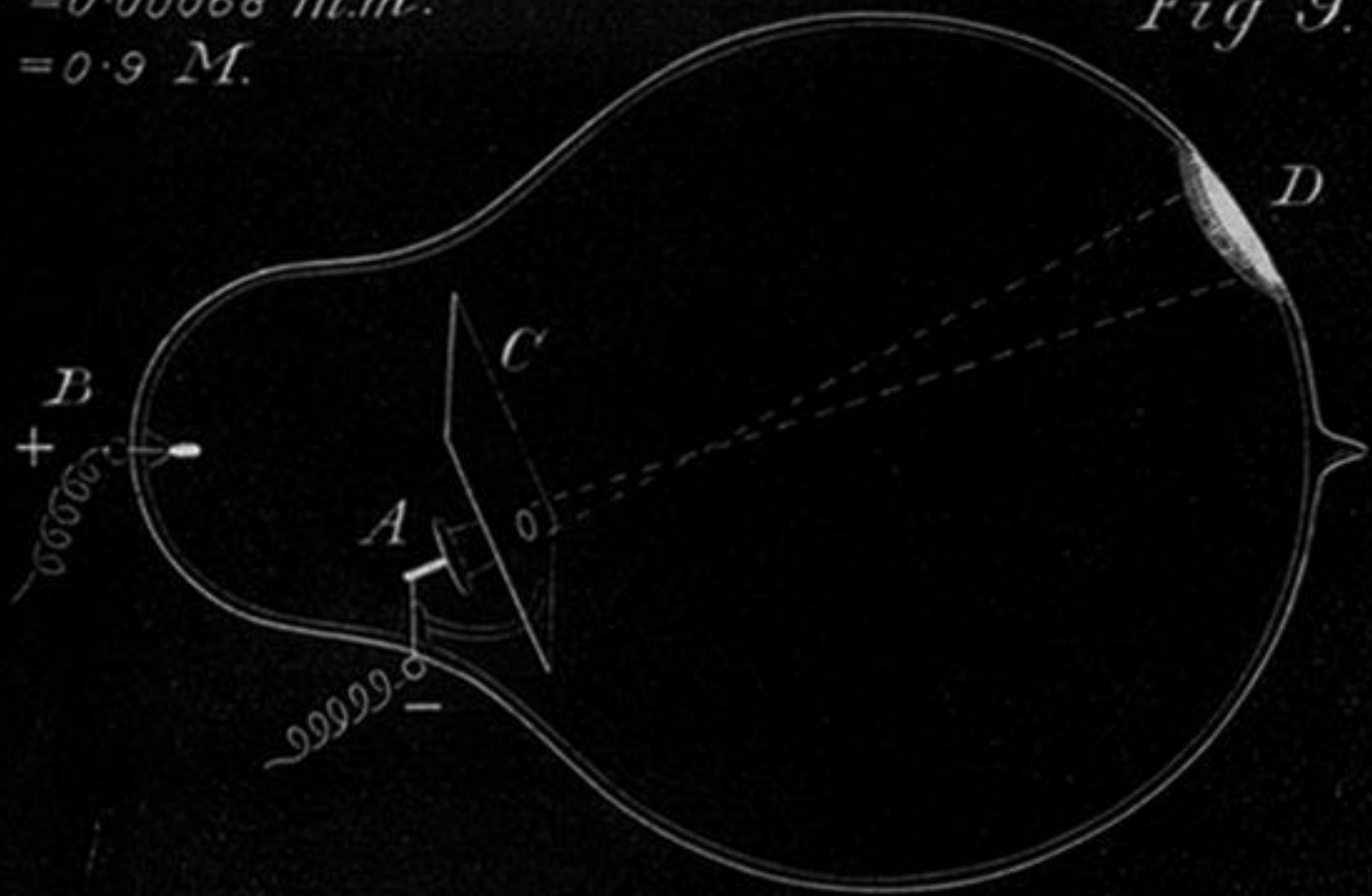


FIG. 8.



$P = 0.00068 \text{ m.m.}$
 $= 0.9 \text{ M.}$

Fig 9.



$I^p = 0.00068 \text{ m.m.}$
 $= 0.9 \text{ M.}$

Fig 10.

