III. "Studies on the Electric Arc." By Professor JAMES DEWAR, M.A., F.R.S., Fullerian Professor of Chemistry at the Royal Institution. Received January 8, 1880.

In a former communication on the formation of hydrocyanic acid in the electric arc, a more complete examination of the various reactions taking place in the arc with poles of various kinds, and in presence of different gaseous media, was promised.

Various difficulties have impeded the satisfactory progress of the investigation. During the course, however, of numerous experiments, facts of interest have been recorded, which appear worthy of embodiment in a short paper.

Formation of Cyanogen Compounds.

The influence of impurities in the carbon on the production of hydrocyanic acid was first examined. For this purpose, some drilled Siemens' carbons were placed in a porcelain tube, and treated for several days at a white heat with a rapid stream of chlorine, until the greater part of the silica, oxide of iron, alumina, &c., were volatilised in the form of chlorides. Sometimes the carbons had a subsequent treatment with hydrogen, or were directly treated with a current of chlorine while the arc was in operation.

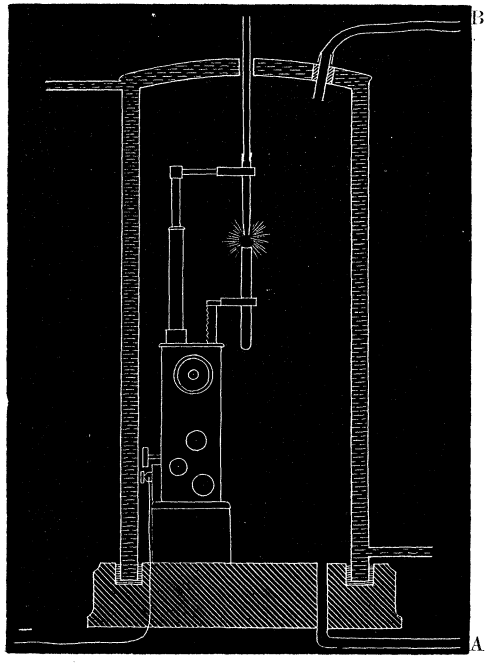
Carbons treated in this way continued to yield hydrocyanic acid, when a steady current of air was drawn through the positive pole as formerly described, even when the same pole had several successive treatments with chlorine during the discharge. Natural graphite poles gave the same result.

As it was evident from the foregoing experiments, that the elimination of a large portion of the impurities had little influence on the production of the hydrocyanic acid, the only other explanation of its formation appeared to be the presence of aqueous vapour, and organic impurities in the air, or a direct formation of cyanogen from carbon and nitrogen. An attempt was made to obtain a pure and dry atmosphere in which such experiments could be carried out. The following apparatus was devised for the purpose.

A tin vessel, fig. 1, about two feet high and one foot in diameter, had an annular space, through which a constant stream of water was kept flowing. This cylinder was placed upon a porcelain stand, having a narrow groove filled with mercury, so as to make an air-tight joint. The lamp was placed inside this vessel, the wires connecting it with the machine being brought through the bottom of the stand. A tube passed through the porcelain base, which allowed a current of dry air to be forced through the vessel. A small aperture in the top of the tin

vessel allowed the glass tube coming from the positive pole to pass with little friction, through which the products from the arc were drawn. This annular vessel was very convenient, not only for examining the products formed in the arc, but also those formed outside of it, and the water flowing round it served the double purpose of keeping it cool and enabling a determination of the amount of total radiation in heat units to be made.

FIG. 1.



Vessels containing sulphuric acid and phosphoric anhydride were placed inside the cylinder in order to dry the interior as completely as possible.

Numerous experiments made by forcing perfectly dry air into the vessel through the tube A, and drawing it out by the tube B through a weighed sulphuric acid bulb, gave after an hour a few milligrams of water, owing no doubt to some slight defect in the soldering of the tin, which allowed a capillary film of water to diffuse into the interior space.

When the ordinary Siemens' carbons were burnt in this almost dry atmosphere, the yield of hydrocyanic acid was still very marked, purified carbons yielding the same results.

As the yield of cyanogen compounds did not appear to be diminished, and it appeared almost impossible to get the large volume of air in the tin vessel perfectly dry, another plan was adopted. The poles were enclosed in an egg-shaped glass globe about eight inches long and six inches in diameter, thus diminishing the volume of air to be dried and dispensing with the water covering. The globe, balanced by a system of pulleys, was firmly attached to the lower or negative pole, with which it moved without impeding the action of the lamp.

Dry air was sometimes forced through the negative carbon itself, at other times through a glass tube passing up the side of it into the globe, the products being drawn through the positive pole as before.

As the globe soon became intensely heated, and as a far larger supply of dry air was forced in than was drawn out, it is inconceivable that any moisture could remain near the arc after it had been burning for a few minutes.

Seven consecutive experiments, each of ten minutes' duration, made with the same purified carbon poles, did not show any diminution in the quantity of hydrocyanic acid, unless in one of the experiments, when the arc would not be drawn into the interior of the carbon tube, but persisted in rotating round it.*

The inference drawn from these experiments was, that the drilled carbons, even after prolonged treatment with chlorine, still contained a quantity of combined hydrogen, and a few organic analyses showed that the amount of ash and combined hydrogen in the various samples was never less than about 0·75 of the former and as much as 0·1 of the latter. Poles made with especially purified carbon by Messrs. Siemens for these experiments proved to be no better in respect to the quantity of hydrogen and ash they contained.

The well-nigh impossible problem of eliminating hydrogen from masses of carbon such as can be employed in experiments of this kind, proves conclusively that the inference drawn by Mr. Lockyer,† as to the elementary character of the so-called carbon spectrum from an examination of the arc in dry chlorine, cannot be regarded as satisfactory, seeing that undoubtedly hydrogen was present in the carbon, and in all probability nitrogen in the chlorine.

Experiments with Carbon Tubes.

In order to ascertain whether the formation of hydrocyanic acid and acetylene in the arc was really due to transformations induced by some

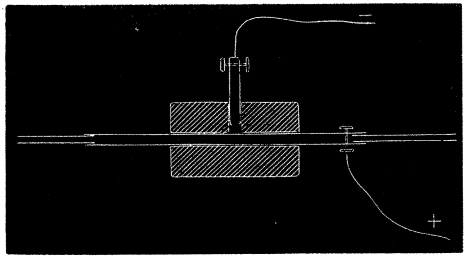
* Cyanogen is difficult to recognise in presence of prussic acid when in small quantity, especially when impurities from the carbons complicate the tests. In speaking generally of the formation of this acid in the arc, I do not mean to exclude the possibility of cyanogen being formed as well.

† "Note on the Existence of Carbon in the Coronal Atmosphere of the Sun." "Proc. Roy. Soc.," vol. xxvii, p. 308.

occult power located in the arc, or was simply the result of the high temperature attained by the carbons, a series of experiments was made in carbon tubes, the arc being merely used as a means of heating. The following is the method of arranging the arc for this experiment.

A block of limestone about five inches long by three inches thick was drilled horizontally as shown in the drawing, another hole being drilled so as to meet it in the centre of the mass.

FIG. 2.



A drilled purified carbon was placed in the horizontal channel and made the positive pole, the negative pole being a solid rod of carbon passing through the vertical aperture. Gases were passed through the positive carbon, and were thus subjected to the intense heat of the walls of the tube, the arc passing outside.

The walls of the positive carbon burnt through with great rapidity, not lasting as a rule more than fifteen minutes. This action could only be prevented by using much thicker carbons, and consequently reducing considerably the intensity of the heat.

The porosity of the carbons, which allowed a constant diffusion of gases through their walls, was another source of difficulty, which has now been overcome.

On passing a mixture of three volumes hydrogen and one volume nitrogen thoroughly dried through the positive pole, a large yield of hydrocyanic acid was always obtained, and on using equal volumes of hydrogen and nitrogen the quantity was if anything increased.

Pure dry hydrogen by itself gave a trace of hydrocyanic acid, and a considerable quantity of acetylene.

Pure dry air gave no hydrocyanic acid or acetylene; moist air, on the contrary, giving abundance of the former, but only a trace of the latter.

The yield in all these experiments altered considerably with the rate at which the gases were passed, a quick stream always producing more than a slow one, unless when oxygen was present.

Formation of Nitrites in the Arc.

In these experiments the annular vessel was made use of, in which

the lamp was allowed to work automatically, often for an hour or two together. A continuous stream of dry air was kept circulating through the interior, being afterwards passed through a series of wash bottles containing dilute caustic soda, or directly through strong sulphuric acid, to absorb the oxides of nitrogen. The nitrous acid was estimated in the former case by titration with permanganate of potash, and the total combined nitrogen by the mercury process.

In this way many experiments were made with a Siemens lamp, both with a long and short arc; Jablochkoff's candles without any insulating material were also employed with the highest intensity current of a De Meritens machine, in order to have the greatest variety in the character of the discharge.

The stream of dry air was forced through at varying degrees of speed, and was found to have a decided effect on the quantity of nitrites produced, the more rapid stream giving the largest yield of nitrites.

The following tables give the quantity produced in a number of different experiments.

The nitrites were calculated as HNO_2.

1. Siemens' machine and lamp. 2. Jablochkoff's candles.

	Nitrates produced in 1 hour.		De Meritens' highest intensity current.
	Siemens'		
	Long arc.	Short arc.	
	Mgrms.	Mgrms.	Mgrms.
1st experiment .... =	193	28	769
2nd ,, ... =	804	97	723
3rd ,, ... =	618	73	1,225
4th ,, ... =	500	121	548
5th ,, ... =	622	90	955
6th ,, ... =	474	85	1,006
7th ,, ... =	380	..	1,257
8th ,, ... =	459	..	964
9th ,, ... =	..	..	664
10th ,, ... =	..	..	489
11th ,, ... =	..	..	693
=	509 mean	..	930 mean.

In these experiments, the total nitrogen estimated by the mercury process was almost identically the same as the amount of nitrogen obtained by a very careful dilution of the acid in a large quantity of water and titration with permanganate, proving that the main product was nitrous anhydride, which may be explained by the fact that the quantity of oxygen in presence of nitrogen in the immediate neigh-

bourhood of the poles is greatly diminished by the combustion of the carbons, or that the nitric peroxide formed is subsequently reduced by contact with the red hot carbon, or other reducing products.

Fig. 3.

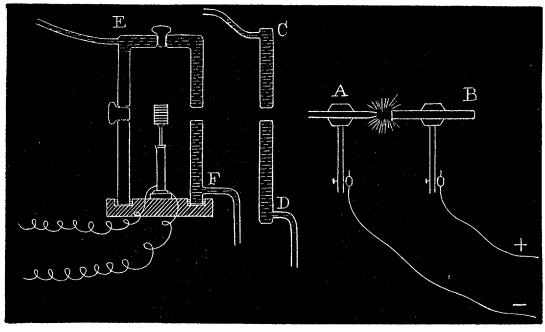
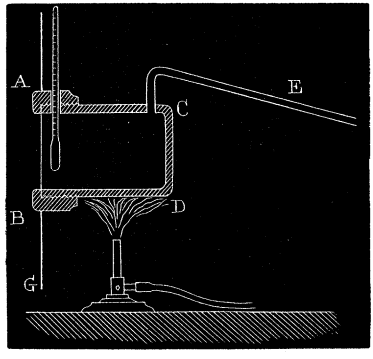


Fig. 4.



Radiation Experiments.

In a report to the British Association* on the determination of high temperatures in the year 1873, it was experimentally proved that the law of Dulong and Petit could not be used for the estimation of high temperatures, seeing that it "gives a far too rapid increase for the total radiation." It was further observed that the variation of the thermo-electric current strength when the same substance radiates at different temperatures, plotted in terms of the temperature, was a

* Report of the Committee for Determining High Temperatures by means of the Refrangibility of the Light evolved by Fluid or Solid Substances. Bradford, 1873. Page 461.

"parabolic curve." Assuming the general accuracy of this law for high temperatures, the total radiation may be taken as nearly proportional to the square of the temperature. From this law the hypothetical temperature of the sun was "estimated as at least 11,000 C." Rosetti has recently made a more elaborate investigation on the subject, and has arrived independently at a formula of a parabolic order. Rosetti * represents his results by the equation

$$\mu = a\mathrm{T}^2(\mathrm{T}-\theta) - b(\mathrm{T}-\theta),$$

where μ is the total radiation measured by thermo-electric current, T° the absolute temperature of the source, θ° that of the medium surrounding the pile, and a and b constants. However well this formula may represent the complete series of the experiments, it is certain that his results for temperatures above 150° may be expressed within the limits of probable error as proportional to the square of the temperature. To be convinced of this, it is sufficient to plot the logarithm of the respective values of the radiation and temperature, when it will be found the results arrange themselves in a straight line, the tangent of which may be 1·9 or 2 for the observations above 150°. Experiments made with the thermopile, surrounded with an annular vessel, through which a continuous current of water at constant temperature is caused to circulate, as represented in fig. 3, where EF represents the section of the vessel, and CD a large water screen, on the same plan, each having a narrow opening, about half an inch in diameter, through which the radiant heat passed to the pile, have confirmed the earlier results. The vessel for holding the mercury or other substance to be heated to different temperatures has a radiating face, which was made of the sheet iron used in the construction of telephone plates, and the thermometer must be placed close to the back of the front surface, and the face guarded with a screen, FG. The tube, CE, is connected with a condenser, when substances at their boiling point are employed for giving fixed points. The form of the apparatus is shown in fig. 4.

This arrangement of the apparatus is necessary in order to get anything like comparable results. The two following tables give the records of two series of experiments, without any correction being made in the numbers representing the deviations of the Thomson galvanometer.

* "Recherches expérimentale sur la Température du Soleil" (Acad. R. dei Lincei. 1877–78).

Table I.

Temperatnre.	Deviation.	Difference.
°		
80	32	
		6·5
90	38·5	
		6·0
100	44·5	
		6·5
110	52	
		7·5
120	59·5	
		7·0
130	66·5	
		9·0
140	75·5	
		9·5
150	85	
		10·5
160	95·5	
		10·5
170	106	
		11·0
180	117	
		13·5
190	130·5	
		13·0
200	143·5	
		14·5
210	158	
		14·5
220	172·5	
		15·5
230	188	

Table II.

Temperature.	Deviation.
°	
100	21
120	29
150	41
160	46
180	57
200	71
220	86
355	240
448	370

If the differences in the galvanometer readings for every ten degrees in the first table be tabulated, it will be observed the second difference may be regarded as constant, considering the errors of observation, so that a parabolic formula can represent the results with sufficient accuracy. These second differences are far more constant than similar numbers deduced from Rosetti's observations, and his more complete formula in terms of the absolute temperature is too extensive, considering the range of the experiments where temperature was accurately known. The results of Table II extend to the boiling points of mercury and sulphur, and the numbers are in near accord with the simple square of the temperature. The alteration in the condition of the radiating surface at high temperatures causes

great complications, and until this difficulty is overcome, experiments at higher temperatures must remain uncertain. All the experiments show that for an approach to a knowledge of temperatures beyond the range of our actual thermometric scale, the law given in 1873 is a sufficiently correct reproduction of the facts, considering the limited data at our disposal.

The intensity of the radiation of the positive pole of the Siemens' arc, as compared with the same surface heated with a large oxy-hydrogen blowpipe, was determined by employing a hollow negative carbon which allowed the intensely heated surface to radiate directly on to the pile, as shown in fig. 3. A large number of observations have been made by this method at different times, and with slight modifications in the order of the experiments, leading to the average result that the intensity of the total radiation of the positive pole of the Siemens' arc is ten times that of the same substance at the temperature of the oxyhydrogen flame. If we take an average result of nine to one, then we may infer that the temperature of the limiting positive pole is about 6,000° C., seeing that the mean temperature of the oxhydrogen may be taken as 2,000° C. The mean value of the total radiation of the Siemens' arc was determined by observing the rate of flow of the water through the annular vessel, represented in fig. 1, together with the mean increment of temperature. This gave on the average 34,000 gram-units per minute, or a little more than three horse-power.

IV. "On the Spectra of Magnesium and Lithium." By G. D. Liveing, M.A., F.R.S., Professor of Chemistry, and J. Dewar, M.A., F.R.S., Jacksonian Professor, University of Cambridge. Received January 8, 1880.

In a former communication ("Proc. Roy. Soc.," vol. xxvii, p. 350) we described our observations on the absorption spectrum of magnesium, and of magnesium with potassium and sodium, as seen in iron tubes in an atmosphere of hydrogen. These absorptions consisted of—

"(1.) Two sharp lines in the green, of which one, which is broader than the other, and appears to broaden as the temperature increases, coincides in position with the least refrangible of the *b* group, while the other is less refrangible and has a wave-length very nearly 5210. These lines are the first and the last to be seen and very constant, and we at first took them for the extreme lines of the *b* group.

"(2.) A dark line in the blue, always more or less broad, difficult to measure exactly.

"(3.) A third line or band, in the green, rather more refrangible

FIG. 1.

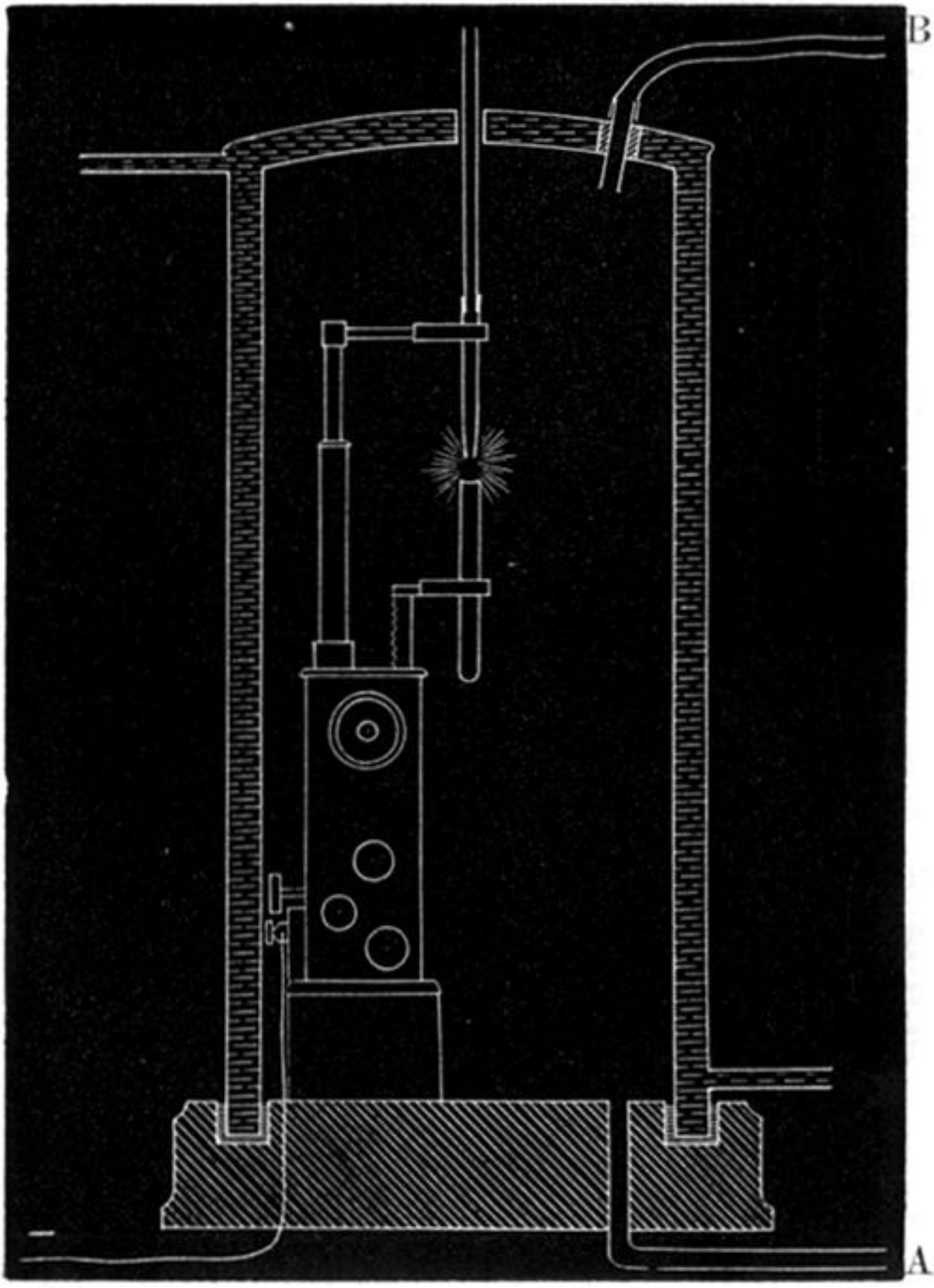


FIG. 2.

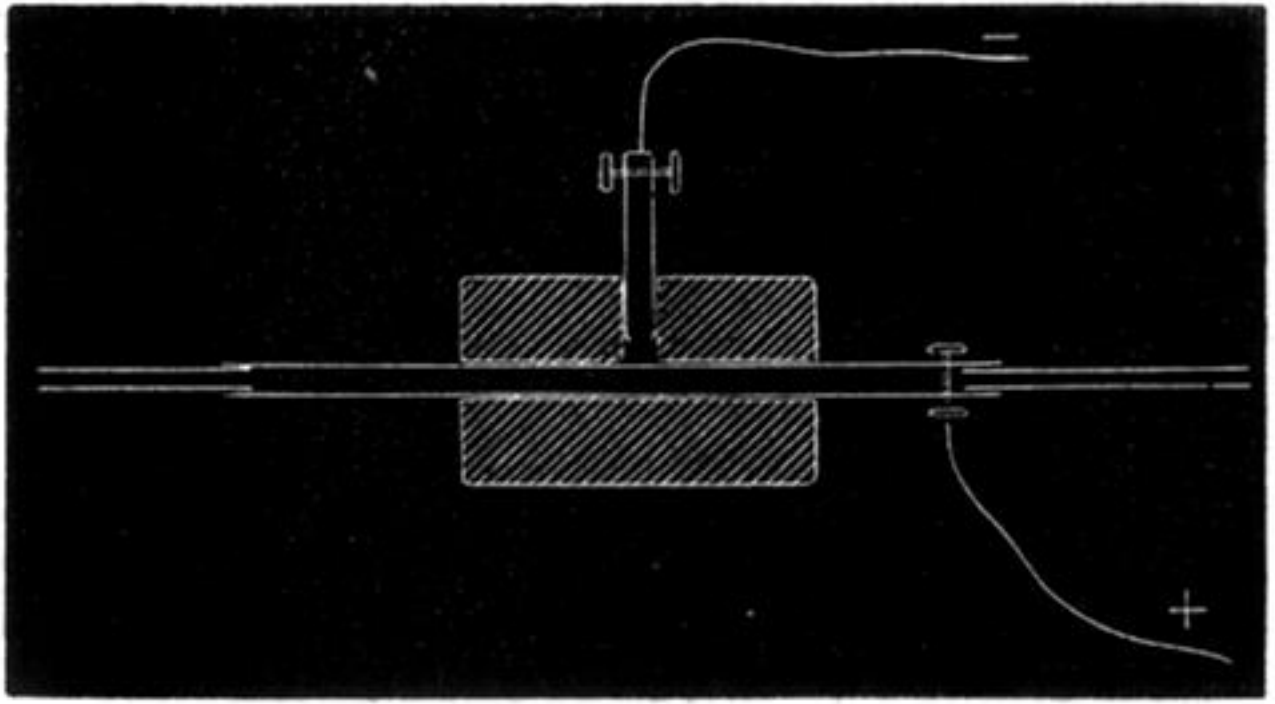


FIG. 3.

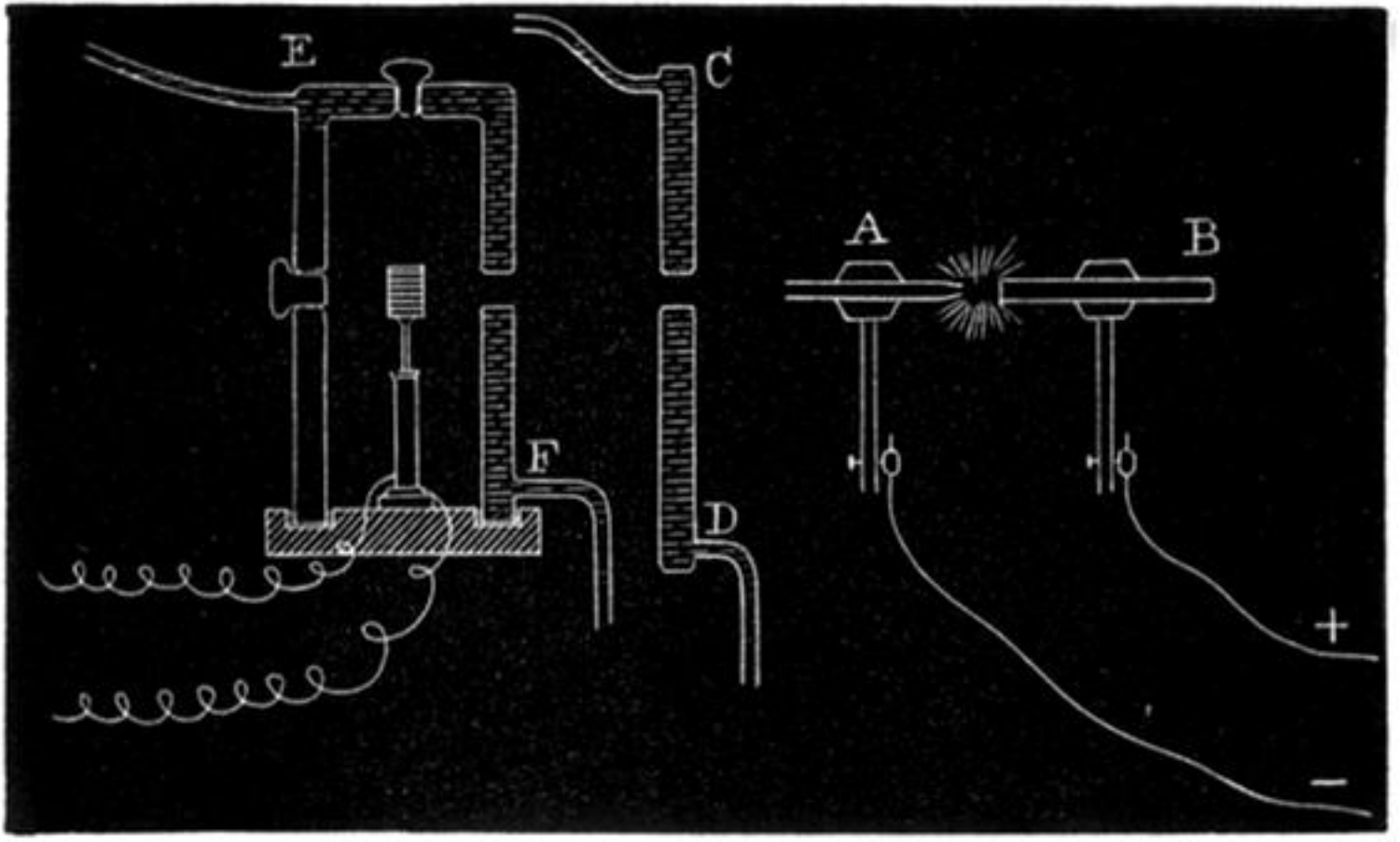


FIG. 4.