fundamental part of the phenomena, the inferences to be drawn from it are probably less important. Chemical action is a constant concomitant in the case; it always took place, 1st, by electrolysis, 2nd, by contact of liberated ions; and, 3rd, occasionally by contact of the original liquids. It sometimes occurs at the meniscus previous to the passage of the current. As also, by the influence of the current, acids and bases are liberated at the contact surfaces, and as in the foregoing numerous experiments with the double and single meniscus apparatuses, the kind of solutions in mutual contact have been found to largely influence the phenomena of the lines, &c., so the layers of new compounds formed by electro-chemical action probably also have similar effects.

From the results of the experiments with the meniscus apparatuses it also appears that the lines may be produced with almost every possible chemical combination of electrolytes; for instance, where the current goes from concentrated to dilute solution, whether from acid salt to acid (as in Experiments Nos. 1, 2, 3, 6, 7, 8, 9, 10, 11, 12, 14, 15, 19, 21, 23, 25, 28, 29, 35, 36, and 38); one acid to another (Experiments Nos. 37 and 41); one alkaline salt to another (Experiment No. 17); an acid salt to a neutral one (Experiments Nos. 4, 13, and 22); a neutral salt to an alkaline one (Experiments Nos. 5 and 44); an alkaline salt to a neutral one (Experiments Nos. 16 and 20); one neutral salt to another (Experiments Nos. 40 and 42); or from an alkaline salt to an alkali (Experiment No. 43); but not so readily from a strong solution of an acid to the same diluted (Experiments Nos. 24, 27, 32, 33, 34, and 39); nor from a strong one of an alkaline salt to the same diluted (Experiments Nos. 26, 30, and 31). A possible relation of the apparent movement of the mass of the liquid to the chemical composition of the two liquids has been already indicated (see p. 68).

"Phenomena of the Capillary Electroscope." By G. Gore, LL.D., F.R.S. Received November 23, 1880. Read January 6, 1881.

In a communication "On the Capillary Electroscope" ("Proc. Roy. Soc.," vol. 30, p. 32), I have described various details necessary to be attended to in the construction and use of a modified form of that apparatus, and I now give an account of an investigation I have made of the phenomena of the movements of the mercury in such instruments. A research I formerly made, "On the Movements of Liquid Metals and Electrolytes in the Voltaic Circuit" ("Proc. Roy. Soc.," vol. 10, p. 235), throws additional light upon the subject. Some of the phenomena arising out of this research have,

for the sake of convenience, been made the subjects of separate communications. (See "Effects of Electric Currents on the Surface of Mutual Contact of Aqueous Solutions," "Proc. Roy. Soc.," vol. 30, p. 322, *ibid.*, vol. 31, p. 250; "Influence of Electric Currents on Diffusion of Liquids;" "Experiments on Electric Osmose;" "Electric Currents caused by Liquid Diffusion and Osmose," *ibid.*, vol. 31, p. 253, *ibid.*, vol. 31, p. 296.)

Erman, in the year 1809, appears to have been the first to observe the movements of mercury in a conducting solution while under the influence of an electric current. Since that time a large number of investigators have examined the phenomenon and the allied ones of electric osmose, electro-capillary action, electric currents produced by capillarity, the mechanical effect of electric currents upon liquids and upon solid particles suspended in them, &c. Among these are Armstrong, E. Becquerel, Buff, H. Davy, Draper, Du Bois Reymond, Faraday, Heidenhain, Hellwig, Herschel, Hittorf, Jürgensen, Kühne, Lippmann, Logeman, Matteucci, Paalzow, Pfaff, Poggendorff, Porrett, Quincke, Reichert, Reuss, Runge, Sabine, Sérullas, Varley, Wheatstone, Wiedemann, and Wright. It is difficult, therefore, to entirely avoid restatement of some of the results arrived at by these investigators.* I have examined the movements in relation to a variety of conditions, some of which, however, are unessential and may be eliminated or diminished. The phenomena have been found to be purely physical, except in those cases where the electricity was of too high tension and produced electrolysis, and in those in which the solution acted chemically upon the mercury.

1. *Influence of the Kind and Strength of the Solution.*

The following experiments were made with the above-mentioned form of apparatus, except in the instances otherwise described. The electric current employed was usually (unless otherwise stated) derived from two wires, one of copper and the other of platinum, each about 1 millim. diameter, immersed about 4 or 5 millims. deep in spring water.

Experiment No. 1.—1 oz. of water, 40 grs. of potassic fluoride. Motion occurred freely, and in the same direction as the current.

Exp. 2.—Various solutions of potassic chloride from 20 to 60 grs. per oz. of water were tried, and in each case the movements of the mercury were in the same directions as those of the current; the former of these solutions was too weak, it offered too much conduction-resistance, and the latter too strong, it clogged the tube. With a solution composed of 1 oz. of water and 40 grs. of potassic chloride in

* A brief translation of the researches of Jürgensen, Quincke, and Wiedemann, may be found in W. A. Miller's "Chemical Physics," 4th edition, p. 530.

a tube of fine bore strong movements occurred, and 85 millims. of extra height of mercury pressure was required to bring the meniscus back to its original position and counterbalance the effect of the current.

Exp. 3.—1 oz. of water and 40 grs. of potassic iodide. The direction of the motion of the mercury agreed with that of the current. 51 millims. height of mercury pressure was required to balance the influence of the current.

Exp. 4.—1 oz. of water and 40 grs. of potassic bromide. All the results the same as those described with the chloride. The current required the pressure of 82 millims. height of mercury to balance it.

Exp. 5.—1 oz. of water and 40 grs. of potassic carbonate. The direction of the movement of the mercury was the same as that of the current. The current required 83 millims. height of mercury to balance it.

Solutions of cyanide of potassium were tried of various strengths from 10 to 100 grs. per oz. of water; the weak ones yielded feeble movements in the direction of the current and the stronger ones clogged the capillary tube.

Exp. 6.—1 oz. of water and 33 grs. of cyanide of potassium in a very fine capillary. An upward current sent the mercury down a long distance and out at the end of the tube. The reverse directions of movement obtained with solutions of potassic cyanide compared with those obtained with dilute sulphuric acid, in capillary tubes, agree with those obtained with the same liquids, and a large globule of mercury in an open shallow dish (see "Proc. Roy. Soc.," vol. 10, p. 235).

Exp. 7.—With a solution of 40 grs. of the cyanide in 1 oz. of water, the movement was more free than with 50 grs. of that salt. By previously passing a downward current, the commencement of motion by the subsequent up-current appeared to be retarded. In another apparatus, consisting of a column of mercury about 20 centims. total height, with a long capillary surmounted by a pressure-chamber quite filled with mercury, and closed by a glass plug, an upward current caused the meniscus to move downwards slowly more than 25 millims., and a downward one raised it about 8 or 10 millims.

Exp. 8.—1 oz. of water and 50 grs. of potassic cyanide. In the fine part of the tube the motion of the mercury was opposite to that of the current, but in the *coarse* part of the tube I noted that it moved in the direction of the current.* When the mercury dropped from the end of the capillary into this solution it formed chains of globules which, when about 2 or 3 millims. high, fell over and formed a heap like a pile of brambles or sticks; the chains of globules did not break.

* This movement requires investigation.

Exp. 9.—1 oz. of hydrocyanic acid ("Scheele's strength") and 40 grs. of potassic cyanide: motion feeble. The directions of motion of the mercury in a capillary of wide bore were the same as those of the current; but in one of narrow bore an upward current sent the mercury freely down. A downward current had but little effect, but on closing the circuit, or on insulating it immediately after an upward current had been passed, the mercury rose instantly.

Exp. 10.—1 oz. of water, 40 grs. of potassic cyanide, and 10 grs. of bicyanide of mercury, formed a very good liquid. The mercury moved in the same directions as the current.

Exp. 11.—1 oz. of water and 40 grs. of mercuric cyanide. A current from copper and platinum wires in dilute sulphuric acid produced little or no movement, but the charge from an ebonite electrophorus (the opposite platinum wire of the electroscope being connected "to earth") caused the mercury to move either up or down in the same direction as the discharge.

Note.—The electrophorus yielded electricity of much too high tension for use with this instrument, especially if the mercury in the capillary tube was the negative pole; gas then quickly collected at the meniscus and stopped the action.

Exp. 12.—1 oz. of water and 40 grs. of mercuric chloride. This solution was unsuitable.

Exp. 13.—A mixture of 7 volumes of distilled water and 3 of strongest aqueous ammonia. The movements were very feeble, but in the usual direction, both with the water-cell and the electrophorus. The mercury would only emerge from the end of the capillary in large drops, not in the usual stream of minute ones, probably in consequence of the small adhesion of aqueous ammonia to mercury (see "Adhesion of Liquids to Mercury," "Phil. Mag.," August, 1863).

Exp. 14.—1 oz. of water and 40 grs. of potassic sulphate. An upward current sent the mercury up freely, and a downward one sent it down. Charging the upper electrode by the electrophorus depressed the mercury as usual; but charging the lower electrode also depressed it, and more strongly. This exceptional effect was obtained several times.

Exp. 15.—1 oz. of water and 40 grs. of potassic borate. The movements of the mercury were feeble, but in the usual direction, both with the current and electric discharge.

Exp. 16.—1 oz. of water and 40 grs. of acid carbonate of sodium. Free movements of the mercury took place in the usual directions, both by the current and the discharge.

Exp. 17.—1 oz. of water and 40 grs. of sulphate of sodium. Feeble movements were produced in the usual directions, both by the current and the discharge.

Exp. 18.—Dilute sulphuric acids of different strengths, varying

from 1 in 40 to 1 in 10. Numerous experiments were made with different forms of apparatus, both horizontal and vertical, employing both the feeble current from the water-cell and the charge from the electrophorus. In every case the movement of the mercury was in the same direction as the current and the electric discharge.

Exp. 19.—1 oz. of water and 10 grs. of boracic acid. Feeble movements occurred in the usual directions with the voltaic current; but charges from the electrophorus, whether applied to the upper platinum wire or to the lower one, depressed the meniscus freely. (Compare Exp. 14.)

Exp. 20.—With strong aqueous acetic acid feeble effects only were obtained, either with the water-cell or electrophorus, but the movements were in usual directions.

Exp. 21.—1 oz. of water and 75 grs. of racemic acid. Rather feeble movements, but in the usual directions, were obtained, both with the current and the discharge.

Exp. 22.—Alcohol. No visible movement was produced by the current from the water-cell, and only a very feeble downward one, by charging the upper electrode with the electrophorus.

Exp. 23.—1 oz. of water and 5 grs. of sodic hyposulphite. The solution was too dilute and was otherwise unsuitable.

Exp. 24.—1 oz. of water and 5 grs. of ammonic alum. Source of current, the water-cell. The movements were very feeble, but in the usual directions; and the downward movements were much more quick and were larger than the upward ones. With 10 grs. of the salt per ounce the movements were more free, but the solution was still too dilute.

Exp. 25.—1 oz. of water and 5 grs. of potassic sulphite. The effects were exactly the same as with the weakest solution of ammonic alum.

Exp. 26.—1 oz. of water and 40 grs. of sulphate of zinc. Free movements occurred in the usual directions.

In the following experiments a drop of dilute sulphuric acid had been previously added to the exciting solution of the voltaic cell.

Exp. 27.—1 oz. of water and 40 grs. of cupric sulphate. Similar results occurred to those with the zinc salt. No signs of deposited copper or of viscosity of the meniscus were produced by the upward current.

The following solutions were also tried:—1 oz. of water as the solvent, and 40 grs. of the solid were employed in each case; ammonia alum; potassic sulphite; potassic sulphocyanide; potassic ferrocyanide; glacial phosphoric acid; sodic nitrate; potassic nitrate; ammonic nitrate; and sodic chlorate. Movements in the usual directions occurred in every instance, and no special phenomena were observable. A solution of 40 grs. of potassic ferrid-cyanide produced a film upon the mercury.

All these experiments show that the movements are greatly affected both by the kind and strength of the solution.

2. *Influence of the Relative Dimensions of the Mercurial Surfaces.*

In order to ascertain whether the movements were dependent upon the circumstance that the mercurial surfaces were of very unequal dimensions, I immersed the extremities of the capillary ends of two vertical electroscopes (of the form I have usually employed) in a solution of 40 grs. of glacial phosphoric acid in 1 oz. of water, with about 10 millims. in length of the capillaries filled with that liquid. I then passed a current (from a large cell of copper and platinum plates in town water) down one capillary tube and up the other; the meniscus descended in the former and ascended in the latter, and in each instrument the motion was just as free as if one of the electrodes had a large surface.

I also passed a current through a short column of mercury in a vertical capillary glass tube between two portions of conducting solution in contact with platinum wires. With a solution of 40 grs. of potassic chloride in 1 oz. of water, both below and above the mercury in a tube of fine bore, and a current derived from the copper and platinum wires immersed in a mixture of 1 volume of sulphuric acid and 19 of water, the mercury moved by a jerk in the direction of the current. To ascertain whether electro-dynamic induction affected the motion in this experiment, I included in the circuit one wire of a double coil of about 1,300 turns of insulated copper wire ("No. 29"), wound upon an iron axis, and closed the secondary circuit. The motion of the mercury was diminished.

The various experiments in which a short column of mercury was between liquids, such as dilute sulphuric acid, solution of potassic chloride or cyanide, in a horizontal capillary, a stronger current was required to move it than when it was in the form of a long column in the usual vertical instrument; it also moved by jerks and only a small distance. A reason why a column of mercury between portions of aqueous solution in a capillary tube of the usual diameter, required a current of greater electromotive force to move it, was probably because the longer total length of the slender column of solution offered much greater conduction resistance.

With a solution of 1 oz. of water, and 33 grs. of cyanide of potassium at each end of a column of mercury about 25 millims. long in a coarse and horizontal capillary tube, with platinum electrodes, and a much stronger current from the copper and platinum wires immersed in a solution composed of 60 grs. of cyanide of potassium and 1 oz. of water, the mercury moved to and fro, each way about 25 millims., and in reverse directions to those of the current. The mercury would not move by the influence of a current from the same

wires excited by a mixture of 1 volume of sulphuric acid and 19 of water. I ascertained by experiment that the former current had the greatest electromotive force.

1 oz. of water and 40 grs. of potassic cyanide, and a current from copper and platinum wires in the solution of cyanide (60 grs. per oz.) above mentioned. With a short length of mercury in a horizontal tube less coarse than the last, the mercury moved in each direction opposite to the current a distance of about 13 millims.

Also by employing a platinum electrode without any mercury upon it, below the vertical capillary, all the movements occurred as usual. These latter experiments prove that the lower electrode need not be composed of a fluid metal, and therefore that I might have omitted to make the previous one respecting the influence of relative dimensions of the two mercurial electrodes.

3. *Influence of Molecular Structure, Cohesion, Liquidity, Viscosity, and Pressure upon the Movements.*

That the molecular structures of the mercury and solution affect the phenomena is quite certain, because we know that the physical properties in general of substances depend essentially upon their internal architecture; the intimate structure of bodies, however, is so inscrutable, that investigation has not yet disclosed it clearly to us. As a solid metal in place of the mercury will not admit of either of the movements, the molecular motion in each liquid is a *relative* one; the motion of the one liquid depends upon the liquid state of the other. The movement is also dependent upon the kind of molecular structure of the solution: 1st, because it varies in direction with a variation in the kind of solution: and 2nd, because it varies also with a variation of strength of the solution; and in each case without any evidence of chemical or electro-chemical action.

Cohesion of the mercury influences the movements, and tends to cause that substance to move more readily from a narrower to a wider part of the tube than in the reverse direction.

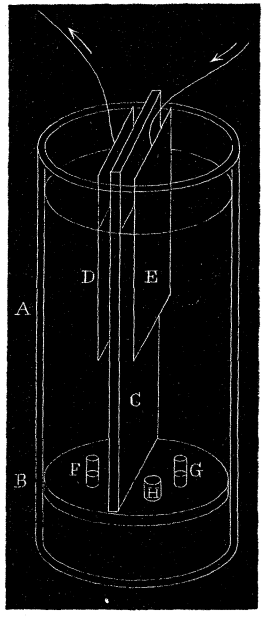
As the liquid state of the lower electrode was not a necessary condition of the motions, the movement of one electrode is not at all dependent upon a similar movement of the other. A single liquid electrode is sufficient to exhibit all the phenomona. Fused salts might probably be used with success, instead of aqueous solutions. (See "Movements of Liquid Metals and Electrolytes in the Voltaic Circuit," "Proc. Roy. Soc.," vol. 10, par. 10.)

The movement was constantly found to diminish as the viscosity of the solution was increased beyond a certain point, by addition of saline or other solid or viscous substance. Pressure probably has but little influence, because liquids are so slightly compressible.

4. Relation to Immiscibility of the Liquids.

Is it a necessary condition of the movements that the two liquids must be incapable of mixing with each other? In the year 1859 (see "Proc. Roy. Soc.," vol. 10, p. 235, par. 9) I made some experiments bearing upon this question: "1st, a definite layer of oil of vitriol was placed beneath a layer of distilled water weakly acidulated with sulphuric acid, and the terminal wires (from a voltaic battery) immersed in the upper liquid; no visible movements occurred at the boundary line of the two liquids; 2nd, a dense solution of cyanide of potassium was placed in a small glass beaker, a few particles of charcoal were sifted upon its surface, and a layer of aqueous ammonia half an inch deep carefully poured upon it. A vertical diaphragm of thin sheet gutta-percha was then fixed so as completely to divide the upper liquid into two equal parts; the vessel was placed in a strong light, and two horizontal platinum wire electrodes from sixty-six pairs of freshly charged Smie's cells immersed one-eighth of an inch deep in the liquid ammonia on each side of the diaphragm. A copious current of electricity circulated, but no movements of the liquids at their mutual boundary line could be detected. A small globule of mercury placed in the lower liquid at once produced evident signs of motion."

FIG. 1.



In order to test in a more searching manner whether during the passage of an electric current movements occur at the boundary surfaces of two liquids which are miscible with each other, similar to those which take place at the mutual surfaces of a liquid metal and electrolyte; and also to ascertain whether any translation of the mass of an aqueous solution occurred similar to the bodily movement of the mercury, I employed the following apparatus (see fig. 1).

A is a thick glass cup about 4 centims. wide and 10 centims. high, having an accurately and tightly-fitting horizontal division of gutta-percha B; also a similarly well-fitting vertical one C. D and E are electrodes of sheet platinum. F and G are thin glass tubes about 10 millims. high, and 3 millims. diameter, open at both ends, and fixed liquid-tight in holes in B. H is a plug of beeswax.

In preparing to use this apparatus, the division B was first fixed in water-tight, the space below it filled with a nearly saturated aqueous solution of cupric nitrate, and the plug H inserted; the height of liquid being adjusted so as to be about half way up the glass tubes. Corks fixed upon the ends of platinum wire were now placed in the tubes. The glass vessel was then nearly filled with a mixture (at 60° F.) of one measure of sulphuric acid and 10 of water; the electrodes immersed; the division C inserted and made as water-tight as possible; and the corks removed very carefully.

An electric current from a single series of five or six Grove's elements of one pint capacity each being now passed through the liquids, the cupric solution appeared to *descend* slowly in one tube, and ascend in the other, moving in the same direction as the positive electricity, and occupying a period varying from five to twenty minutes for the movement. As the phenomena observed in this kind of experiment were considerably different from those observed with mercury in capillary tubes, I have made a separate examination of them under the title of "The Influence of Voltaic Currents on the Diffusion of Liquids" ("Proc. Roy. Soc.," vol. 31, p. 250). As also I could not readily obtain definite lines of separation of two miscible liquids in tubes of as small a diameter as those employed with mercury, I have been unable to solve as satisfactorily as I could have wished the question whether perfect immiscibility of the liquids is a necessary condition of the movements of the mercury in such experiments; Herschel stated ("Phil. Trans.," 1824, p. 189) that it is.

5. *Relation of the Movements to the Volume and Specific Gravity of the Mercury.*

In order to ascertain whether the whole of the mercurial column moved in the direction of the motion of the meniscus, or expanded and contracted coincident with the advance and retreat of that surface, I

made experiments with a series of different capillary electroscopes in a *horizontal* position, taking care to remove an additional part of the apparatus in each successive experiment:—

The first electroscope (No. 1) consisted of two similar capillary tubes, inserted in two pressure-chambers, connected together in a direct line by a long straight glass tube of narrow bore, each chamber being provided with a platinum wire terminal. The chambers, connecting tube, and capillaries were filled with mercury; air was excluded, and the ends of the capillaries were immersed as usual in dilute sulphuric acid containing electrodes of mercury. In the second apparatus (No. 2) the intermediate glass tube was removed, and a single pressure-chamber, 60 centims. in length (with a platinum wire at each end), was used in its stead. In a third (No. 3), the chamber was reduced to a length of about 8 centims., and had a platinum wire at each end. In a fourth (No. 4), the chamber was removed altogether, and the central tube and capillaries were formed of a single piece of glass, the middle part being about 4 centims. long, of the usual diameter and bore, and having a fine wire of platinum sealed into it as an electrode.

I also made experiments with a series of electroscopes in a *vertical* position, each successive apparatus being increasingly simple, and each closed at the upper end and perfectly filled with mercury, except the lower end containing the electrolyte.

The first (No. 1*a*) consisted of the capillary (dipping as usual into dilute sulphuric acid with a mercury electrode), short pressure-chamber, and a long glass tube above it, closed at the top by a thick india-rubber tube and a strong pressure-clip. In the second (No. 2*a*), the long glass tube was dispensed with, and the upper end of the pressure-chamber was closed by a glass plug. In the third (No. 3*a*), the chamber was excluded, the platinum wire electrode being melted into the side of the large part of the glass tube, and the upper end of that tube drawn out to a fine point, and closed by melting sealing-wax whilst mercury was exuding from it. The fourth (No. 4*a*) was similar to the third, except that the upper end was closed by fusing a part of the fine tube itself whilst it was filled with mercury. And in a fifth (No. 5*a*), the bulky portion of the glass tube was dispensed with by fixing an extremely fine platinum wire in the somewhat larger and upper part of the capillary by fusion.

In all the experiments made with these different instruments, whether horizontal or vertical, the electrolyte used was a mixture of 1 volume of pure sulphuric acid and 14 of water, and the voltaic current employed was that already mentioned (see p. 86). In each of the experiments with them the mercury moved in the same direction as the current, whether that was towards the point of the capillary tube or the reverse. In many of the experiments a charge from an

ebonite electrophorus was used as the source of electricity, and in these cases also the mercury moved in the direction of electric discharge. With the horizontal electroscopes (all of which were open at both ends), the mercury only moved at that end at which the current or discharge passed; but if the current or discharge passed at both ends simultaneously, then the mercury moved at both ends simultaneously, whether the electric flow was from end to end, from both ends to middle, or from middle to both ends (provided it was free to move), and the directions of the motion in the two ends agreed with the above general statements.

In these various experiments the amount of capillary movement with a given current did not appear to vary greatly with the total bulk of mercury in the entire apparatus.

The displacement of volume of the mercury being so extremely small, it may be accounted for on the supposition that minute traces of air (not visible by means of an eye-glass) adhere to the sides even of the smallest and most perfectly prepared tubes; and when by the action of the current or discharge, the meniscus is caused to approach the capillary orifice, these minute portions of air become rarefied. This view is supported by the facts, that traces of air are continually observed in the capillaries, and also that when the apparatus was reduced to its simplest form and smallest size, as in No. 5*a*, the motion of the meniscus appeared to be somewhat less free.

From these results, I consider it improbable that the movements are to any large extent attended by a change of volume of the mercury.

6. *Influence of Adhesion, Capillarity, and Surface Tension.*

In a paper "On the Adhesion of Liquids to Mercury" ("Phil. Mag.," vol. 26, 1863), I have stated that "if a drop of Nordhausen sulphuric acid, about one-tenth of an inch in diameter, is carefully placed by means of a glass rod upon the centre of a clean globule of pure mercury, about 80 grs. in weight, it instantly diffuses itself in a thin film over the surface of the metal, and the mercury becomes flattened, and exhibits vertical movements all over its surface; but if the experiment is made with a strong aqueous solution of ammonia or of caustic potash, no such results occur, the alkaline solution contracts itself into a spherical form, and persistently floats to the side of the mercury without spreading itself over the surface."

This circumstance, viz., the small adhesion of aqueous ammonia to mercury, is probably connected with another already mentioned (see p. 88), viz., that when the mercury was caused to flow out of the end of the capillary tube into a solution of ammonia, it would only emerge in large drops instead of the usual stream of minute ones. Difference

of degree of adhesion of different solutions to mercury, however, will not by itself account for the movements.

Further, it is well known that if a drop of water is placed upon a horizontal surface of mercury, and an electric current passed from the mercury into the water, the two liquids spread out, whilst if the current is reversed the water contracts, as if in the former case the adhesion between the two substances was increased, and in the latter decreased; and various interpretations have been given of these phenomena (see Sabine, "Phil. Mag." vol. 2, 1876, Supp., "On Electricity disengaged between Mercurial Surfaces"; section 2). I have repeated this experiment: 1st, with dilute sulphuric acid, the effects were the same as with water; 2nd, with a solution of potassic cyanide and a downward current the solution spread out, and with an upward current no such effect was manifested; and 3rd, with one of potassic carbonate the solution spread out, both with an upward current and with a downward one, most with the former. These changes of adhesion of liquids to each other by electric influence cannot alone produce the to-and-fro movement in the electroscope, because no action between two bodies could cause both of them to simultaneously advance or retreat together in the same direction.

These apparent changes of adhesion of liquids to each other by the influence of electric currents are, however, essentially similar to the phenomena under consideration, and agree with the chief and wider truths of electrolysis, viz., that when a metal is made positive to a liquid by the passage of an electric current from the former into the latter, there is usually excited a tendency to union of the two bodies; and that, when made negative by a current, an opposite tendency is excited. They also agree with the fact that if, whilst mercury is slowly issuing from the end of the electroscope into a solution, the mercury is rendered positive to the liquid by the passage of an electric current, the rapidity of flow of the metal is usually increased, while, if it is rendered negative, the flow is usually decreased. The degrees of rapidity of flow of mercury from the end of a capillary glass tube into different electrolytes, with and without the simultaneous passage of an electric current, might form a subject of investigation.

That the phenomena of the electroscope are largely affected by the adhesion of the liquids to the tubes, especially when the movements of the liquids take place in capillary tubes of extremely small diameter, does not admit of doubt, because the magnitude of the surfaces of adhesion then bear a larger proportion to the mass of the liquid in the capillary. It is well known that some of the most fundamental properties of liquids are changed whilst under the influence of adhesion in capillary spaces. For instance, Melsens found that, notwithstanding the great volatility of bisulphide of carbon when alone, it required more than an hour to expel 2 or 3 cub. centims. of that liquid from

a mixture of 30 grms. of charcoal and 23 cub. centims. of the sulphide contained in a glass tube immersed in boiling water (see "Phil. Mag.," July, 1877, p. 43).

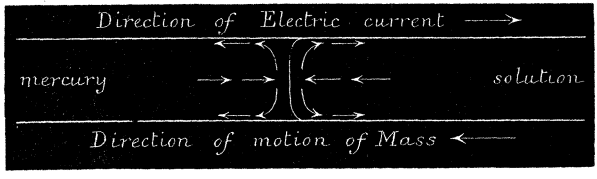
It is evident also that the movements must be greatly affected by the relative degrees with which each of the liquids adhere to the containing tube, and it is not improbable that as the aqueous solutions adhere to the glass tube and the mercury does not, the latter yields to the moving influence to a very much greater extent than the former, and that the motion is chiefly (if not wholly) produced through the agency of the adhesion of the solution to the tube, and not so much through that of the mercury.

Although the motion is frequently prevented by adhesion of the mercury to the tube, it is not caused simply by diminution of that adhesion whilst under the influence of the current, because if that did occur, it could only operate by allowing some dynamic cause to produce the motion.

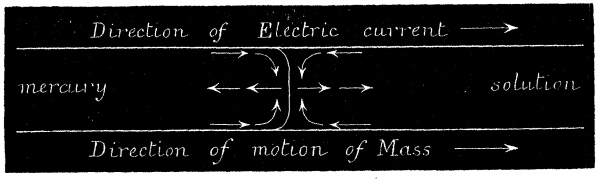
The evidence with regard to adhesion supports the hypothesis that the motion is primarily due to a direct mechanical action at the immediate surfaces of contact of the mercury and solution, producing movements of solution and mercury in directions agreeing with those in the annexed figures;* and the to-and-fro movement of the mass is

FIG. 2.

In KCy solution.



In dilute sulphuric acid.



a secondary circumstance, arising from the former in consequence of the greater adhesion of the solution than of the mercury to the tube.

* The repulsive action being usually at the negative pole in liquids, is a similar fact to the molecular repulsion of highly rarefied gases at the negative electrode in Mr. Crookes's experiments.

The mechanical law of action and reaction of equal and opposite forces also requires the primary movements of the mercury and solution to be in opposite directions. If this hypothesis is correct, the unequal adhesion of the mercury and solution to the glass is a necessary condition of the simultaneous advance of the two liquids in the same direction. If the tube was as free to move as the liquids, it would of course move in an opposite direction to them. The number of physical actions, however, involved in the case is probably much greater than is represented by the above explanation.

Herschel observed that "the peculiar action is only exerted at the common surface of the fluids;" and nearly all the evidence supports the conclusion that it is primarily an action of films and not of the mass of mercury or of solution within the capillary tube.

Even when during the passage of a current, the column of liquid is prevented by adhesion from rising or falling in the capillary tube, there is probably a motion occurring in the contiguous portions of the mercury and solution, though not usually visible even by the aid of a microscope.

Armstrong's experiments ("Phil. Mag." vol. 23, 1843, pp. 194–202) also indicate that the movement of the mercury is affected by an action of adhesion between the surface of the liquid and glass within the tube, because in his experiments, when the silk thread, acting as a fulcrum, was removed, the amount of liquid flowing in one direction was equal to that flowing in the other, and there was no manifest transfer of the mass.

In all cases with a globule of mercury in a pool of liquid, the outer film of mercury and the film of liquid in contact with it appears to move in the same direction; the mass of the liquid, and also that of the interior of the mercury, must, therefore, of necessity, move in a direction opposite to that of the films (compare Herschel, "Phil. Trans." 1824, p. 165).

The opposite movements obtained with dilute sulphuric acid and with solution of potassic cyanide might also be explained on another supposition, viz., that one of these liquids adheres more strongly, and the other less strongly, than mercury to glass; but this does not appear to be a fact.

Although the phenomenon of to-and-fro motion appears to be essentially due to a combination of surface actions, it is not confined entirely to capillary spaces, the motion (as is well known) takes place as readily with a large globule of mercury in a pool of liquid as in a capillary tube. (See also "Movements of Liquid Metals and Electrolytes in the Voltaic Circuit," "Proc. Roy. Soc.," vol. 10, par. 35.) The to-and-fro movement, in the case of a globule of mercury in a pool of liquid, is dependent upon the circumstance that the solid surface of the containing vessel, upon which the mercury and film of

solution beneath it lie, constitutes a fulcrum upon which the moving layers of liquid mechanically act. If it were possible to suspend the mercury in the midst of a large mass of a liquid electrolyte of its own specific gravity, the effects would probably be greatly modified, and there would be very little translation of the mass of mercury (compare Herschel's paper, section 10, p. 167).

In the experiments by Armstrong, also those of Quincke and Jürgensen, of the mechanical transfer of liquids by the passage of electric currents through slender columns of them in tubes, the axial portion of the liquid was observed to move in an opposite direction to the outer layer. This inner moving portion, or that farthest away from the surfaces of adhesion, may be regarded as the return current.

It is generally considered that the surface layer of particles of every solid and liquid is in a state of mechanical tension, and consequently that every mass of such substance, even that which is only of microscopic magnitude, may be crudely viewed as being bounded by a more or less tightly-fitting envelope. This circumstance also appears to be related to the phenomenon of motion of the mercury. The surface tension of that metal appears to be lessened at the positive mercurial electrode, and increased at the negative one in nearly all electrolytes. As there is also a surface tension of the liquid as well as that of the mercury, the primary motion is probably a resultant of the two. According to this view there exists *two* modes by which an electric current may vary the surface tension of a conductor in contact with an electrolyte, the one being attended by electrolysis, and the other not. If it were simply a result of diminution of surface tension of the mercury by the passage of an outgoing current, then it ought not to vary in direction by variation of liquid, strength of liquid, or diameter of tube.

As adhesion influences so greatly the action of the instrument, perfect freedom from dust is a most important condition of success, and the most effectual way of securing this is to insert the capillary tube in the pressure-chamber as soon as it is made, and fill it at once with clean mercury. Multitudes of points of adhesion are met with in tubes which have long been open to the atmosphere. The pressure tube should also be completely freed from dust by previously agitating successive portions of mercury in it. Dust, not moisture, is the great source of failure. Adhesions of the mercury do not usually interfere unless they happen to be within the range of movement of the meniscus.

The influence of friction I have not examined; it plays, however, an important part in the practical use of the instrument.

7. *Relations of the Movements to Heat and Temperature.*

As heat, applied to the junction of mercury and an electrolyte,

produces an electric current, it is reasonable to infer that an electric current passed through such a junction in the same direction as the one produced, would tend to lower the temperature. And as it is well known that both the cohesion of liquids and their elevation are diminished by rise of temperature, it is probable that the electric current, by producing a minute change of temperature at the junction, affects to a slight extent the capillary elevation. By comparing, however, the directions of the electric currents obtained by heating mercury in contact with various solutions which exercise no chemical action upon it (see "Thermo-Electric Behaviour of Aqueous Solutions with Mercurial Electrodes," "Proc. Roy. Soc.," vol. 29, p. 472), with the directions of movements produced by given directions of electric currents in the same solutions in these experiments, it may be perceived that they do not to any large extent coincide.

That the mercury should also conversely suffer slight changes of temperature by electro-capillary action, is in accordance with the discovery made by Pouillet ("Ann. de Chemie et de Phys.," vol. xx, 1822, pp. 141–162), that heat is evolved by the capillary absorption of liquids by solids; and with the experiments of Jungk ("Phil. Mag.," vol. 2, 1876, p. 454; and "Pogg. Ann.," vol. cxxv, p. 292), and further, with those of Melsens, who states that by mixing 4·45 grms. of charcoal and 33 of bromine, the rise of temperature was 35° ("Phil. Mag.," vol. 2, 1876, p. 454; also "Mém. de l'Acad. Royal de Belgique," vol. xxiii).

The movement is evidently not caused by heat of conduction resistance, because that would produce expansion and advancing motion only. If also the motion is simply due to thermic expansion, then heat of chemical combination at the anode in cases of electrolysis in the capillary ought to cause the mercury to move downwards, but with solutions of potassic cyanide it moves the reverse. The relations of electro-capillary movements to heat require, however, much more investigation.

8. *Relations of the Movements to Electric Conditions.*

The phenomena of the capillary electroscope are not results of electrolysis, nor of disruptive discharge, but of conduction proper, and may occur either with or without electro-chemical change. In nearly all previous investigations of the electric movements of mercury, very much stronger electric currents were employed, and the results were complicated by electrolytic phenomena. That electrolysis, when it does occur, is only a coincident circumstance, is proved by the non-liberation of hydrogen at the meniscus when that surface is made negative in dilute sulphuric acid and in various other solutions; also, by the mercury at the meniscus not becoming viscid when made the negative pole in a solution of cupric sulphate (see

Exp. No. 27); and further, by the surfaces of the meniscus not becoming oxidised when made the positive pole in either of the various solutions usually employed; provided in all these cases that ordinary chemical action is absent and that the current is sufficiently weak.

The reverse directions of movement produced by the same direction of current in dilute sulphuric acid and in solution of potassic cyanide, probably cannot both be explained by the theory that the movements are due to electro-chemical exidation and deoxidation. The upward movement caused by a downward current can hardly be due to electrolysis, because that action, by continually destroying the outer film of mercury, tends to diminish its surface tension.

Being largely dependent upon electric conduction, the amount of movement of the mercury is affected by every circumstance which alters the conductivity. The part of the circuit which offers the greatest amount of conduction resistance is the slender column of solution between the meniscus and the end of the capillary tube; there the resistance is considerable. The nearer, therefore, the meniscus is to the end of the tube, and the shorter the column of solution (as well as that of the mercury), the more rapid is the movement, especially if the tube is slightly larger in diameter towards that end; this circumstance also tends to make the downward movement an accelerated one, even in a tube of uniform diameter, and the upward movement the reverse; and also accounts for the fact that the instrument is more sensitive to a downward current than to an upward one, unless the tube becomes narrower downwards at too rapid a rate.

The secondary current of an induction coil was not suitable for working the instrument, because it produced electrolysis. On many occasions an electrophorus was used as the source of electricity, and this also produced a similar effect. On charging the electroscope with it, either by induction or by contact, the movements were freely produced, provided the electroscope was not insulated. If it was perfectly insulated the movements did not occur, and if it was imperfectly insulated and then charged by momentary contact, the mercury continued to run out at the end of the capillary tube after removal of the electrophorus, and ceased to flow by discharging the instrument.

I made a capillary tube in accordance with the annexed sketch, with a pressure tube A, and a platinum wire electrode Pt; and filled

FIG. 3.

it with mercury whilst in a horizontal position; then melted it off at the point B by means of a minute flame; broke it off at C, and fixed it vertically with its end C in dilute sulphuric acid above an electrode. Not a trace of air was visible in any part by the aid of a strong magnifying glass. By charging the upper electrode by induction with an electrophorus, the mercury descended freely; and by charging the lower one it ascended, provided the free end was not insulated. The motion of the mercury, therefore, is evidently not produced by mere electric charge but requires electric flow.

Even a residual electric charge of the ebonite base of the reverser (see "Proc. Roy. Soc." vol. 30, p. 32) at the surfaces of contact of that substance with the brass fittings which had been connected with the poles of the nearly exhausted little water-cell was sufficient to work the instrument. Also a voltaic current which raised the meniscus 19·5 millims. would not produce a visible movement of the needle of a torsion galvanometer having a coil of 100 ohms resistance. These facts illustrate the extreme sensitiveness of the instrument to electric flow of the feeblest tension; and the apparatus might be used for examining the conductivity proper of electrolytes.

From the results achieved by Quincke ("Pogg. Ann.," vol. cxiii, 1861), and by Jürgensen (Reichert and Du Bois Reymond's "Archiv," 1860, p. 573; also "Chemical Physics," by W. A. Miller, 4th Edition, pp. 530–533), and the various results obtained by myself, I conclude that the primary mechanical movement in the instrument is due to a more or less charged electric state of the surfaces of the liquids and tube. The electric tension accompanying that state alters the degrees of adhesion of the substances to each other, and produces electric convection, which, in consequence of the unequal adhesion of the solution and mercury to the tube, produces a to-and-fro movement of the mass. The less fundamental results, such as reversal of direction of movement with solutions of potassic cyanide, or with tubes of different diameter, would probably be found to be necessary results of the above causes under the altered conditions. A brief translation of Quincke's explanation of somewhat similar phenomena may be found in W. A. Miller's "Chemical Physics," 4th Edition, p. 532.

The primary action appears to consist nearly wholly of a direct conversion of electricity into mechanical power; and this accords with the great sensitiveness of the instrument and the comparatively considerable force of the movements. This force has been already applied by Lippmann in the construction of an electro-capillary engine. The converse action, viz., the production of electric currents by mechanically raising and lowering mercury and an acid solution in capillary tubes, has also been obtained by Lippmann ("Phil. Mag.," vol. 47, 1874, p. 281).

9. *Influence of Chemical Action.*

The movements do not appear to depend upon the chemical nature of the solution, because they take place equally well with acid, alkaline, and neutral liquids. Being also purely physical, they are not dependent upon chemical action; such action, when it does occur, appears in every case to interfere with them.

Note.—Since the publication of a previous communication "On the Capillary Electroscope" ("Proc. Roy. Soc.," vol. 30, p. 32), I have been favoured by M. Lippmann with the following remarks respecting that instrument. "1st. The liquid is to be diluted sulphuric acid, containing something like one-third its weight of sulphuric acid. Weak acid does not film glass properly; most liquids do not; and then stoppages, or a jumping motion of the mercury, occur, such as you have described. 2nd. The capillary tube is to be cut very short (to about 10 millims.), the motions are in that case ten times more rapid than in a tube of 10 centims., because the friction is reduced in that proportion; besides, possibilities for obstruction are reduced also in the same proportion. 3rd. The instrument is only fit for measuring electromotive forces smaller than one Daniell; by using over-great electromotive forces the capillary constant goes over its maximum value, and then the movement of the mercury is reversed as you noticed it to be the case at the end of your communication (see, about this maximum, 'Ann. Chimie et Physique,' 1875, and also 1877). If you will do me the pleasure of visiting M. Jamin's laboratory in the Sorbonne, you will find there several electrometers in good working order; three of these are being used by different observers for separate researches, with a precision of $\frac{1}{10000}$ Daniell."

FIG. 1.

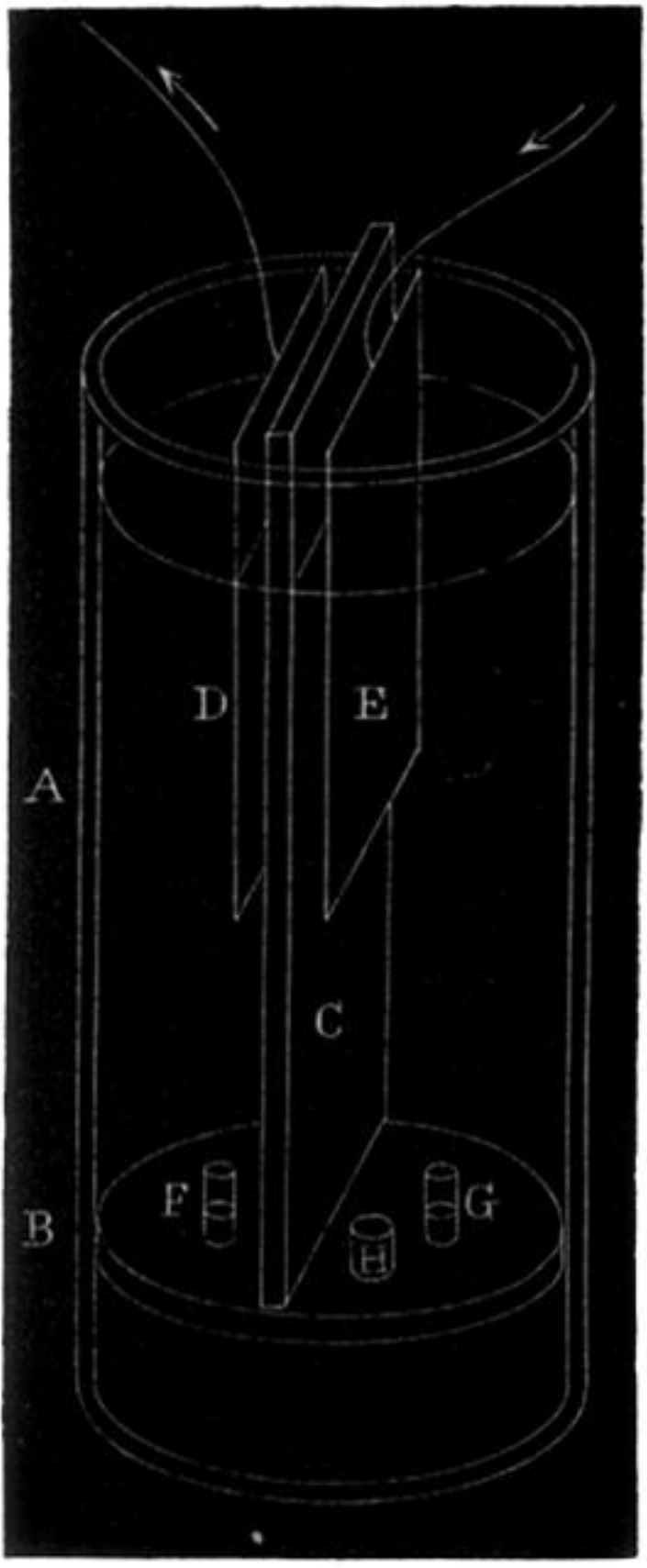
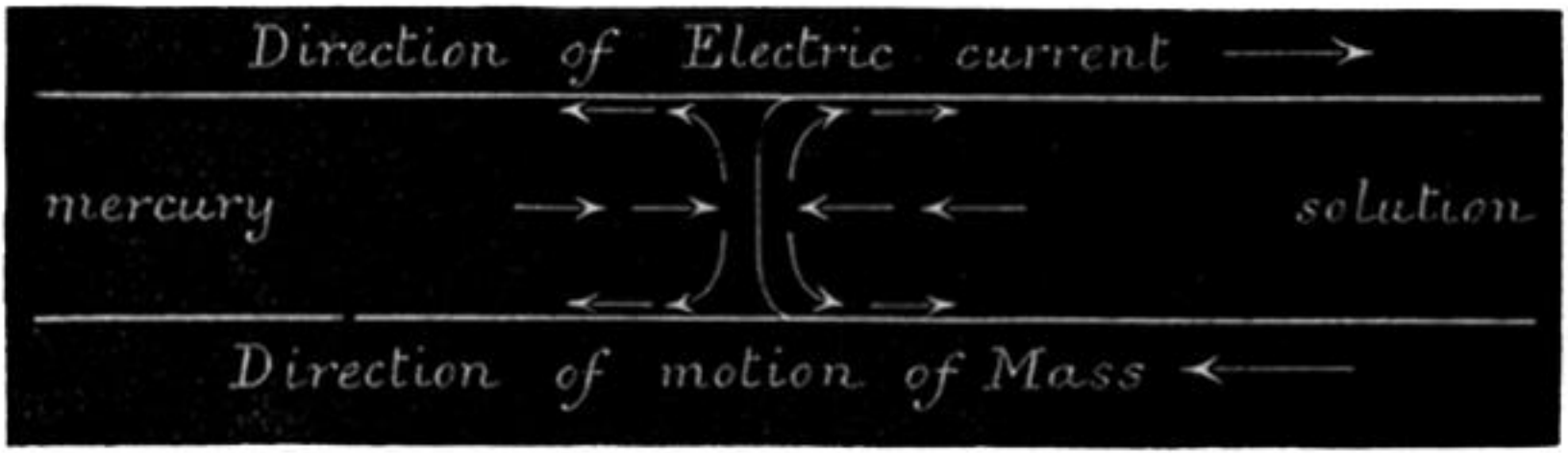


FIG. 2.

In KCy solution.



In dilute sulphuric acid.

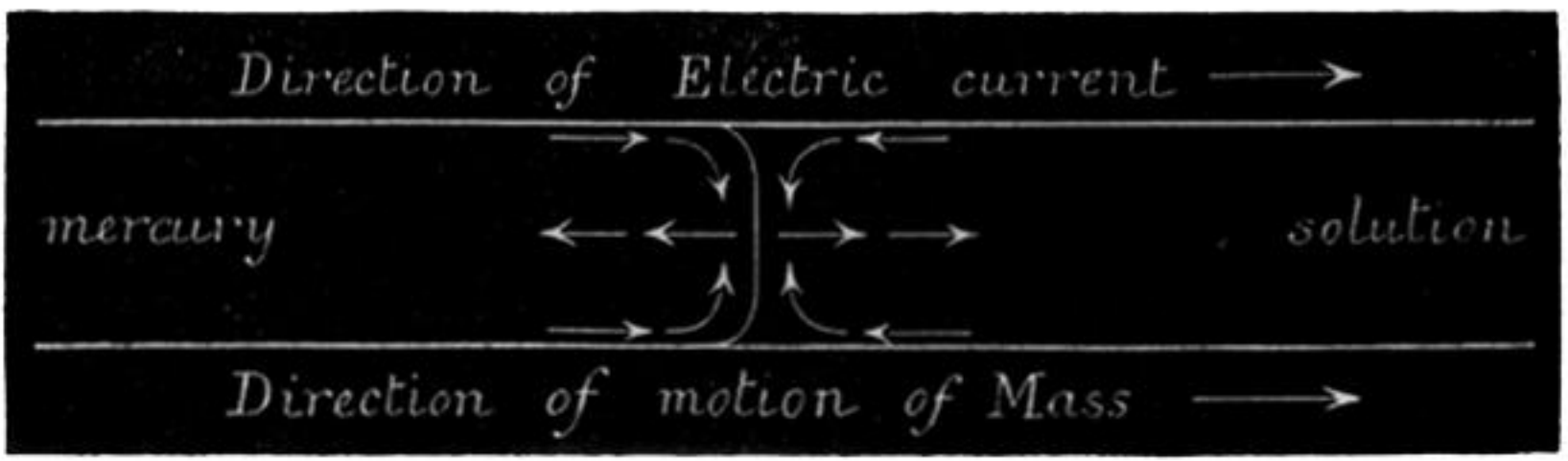


FIG. 3.