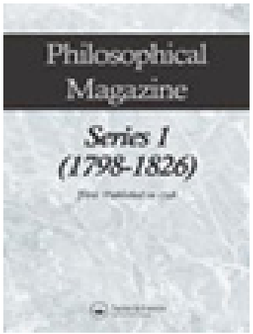

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XXXI. The bakerian lecture, on some chemical agencies of electricity

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XXVI. *The Bakerian Lecture, on some Chemical Agencies of Electricity.* By HUMPHRY DAVY, *Esq.* *F. R. S. M. R. I. A.*

[Concluded from p. 119.]

VIII. *On the Relations between the electrical Energies of Bodies, and their Chemical Affinities.*

As the chemical attraction between two bodies seems to be destroyed by giving one of them an electrical state different from that which it naturally possesses; that is, by bringing it artificially into a state similar to the other, so it may be increased by exalting its natural energy. Thus, whilst zinc, one of the most oxidable of the metals, is incapable of combining with oxygen when negatively electrified in the circuit, even by a feeble power; silver, one of the least oxidable, easily unites to it when positively electrified; and the same thing might be said of other metals.

Among the substances that combine chemically, all those, the electrical energies of which are well known, exhibit opposite states; thus, copper and zinc, gold and quicksilver, sulphur and the metals, the acid and alkaline substances, afford opposite instances; and supposing perfect freedom of motion in their particles or elementary matter, they ought, according to the principles laid down, to attract each other in consequence of their electrical powers. In the present state of our knowledge, it would be useless to attempt to speculate on the remote cause of the electrical energy, or the reason why different bodies, after being brought into contact, should be found differently electrified; its relation to chemical affinity is, however, sufficiently evident. May it not be identical with it, and an essential property of matter?

The coated glass plates of Beccaria strongly adhere to each other when oppositely charged, and retain their charges on being separated. This fact affords a distinct analogy to the subject; different particles in combining must still be supposed to preserve their peculiar states of energy.

In the present early stage of the investigation, it would be

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be improper to place unbounded confidence in this hypothesis; but it seems naturally to arise from the facts, and to coincide with the laws of affinity, so ably developed by modern chemists; and the general application of it may be easily made.

Supposing two bodies, the particles of which are in different electrical states, and those states sufficiently exalted to give them an attractive force superior to the power of aggregation, a combination would take place which would be more or less intense according as the energies were more or less perfectly balanced; and the change of properties would be correspondently proportional.

This would be the simplest case of chemical union. But different substances have different degrees of the same electrical energy in relation to the same body: thus the different acids and alkalies are possessed of different energies with regard to the same metal; sulphuric acid, for instance, is more powerful with lead than muriatic acid, and solution of potash is more active with tin than solution of soda. Such bodies likewise may be in the same state or repellent with regard to each other, as apparently happens in the cases just mentioned; or they may be neutral; or they may be in opposite or attracting states, which last seems to be the condition of sulphur and alkalies that have the same kind of energy with regard to metals.

When two bodies repellent of each other act upon the same body with different degrees of the same electrical attracting energy, the combination would be determined by the degree: and the substance possessing the weakest energy would be repelled; and this principal would afford an expression of the causes of elective affinity, and the decompositions produced in consequence.

Or where the bodies having different degrees of the same energy, with regard to the third body, had likewise different energies with regard to each other, there might be such a balance of attractive and repellent powers as to produce a triple compound; and by the extension of this reasoning, complicated chemical union may be easily explained.

Numerical illustrations of these notions might be made without

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without difficulty, and they might be applied to all cases of chemical action; but in the present state of the inquiry, a great extension of this hypothetical part of the subject would be premature.

The general idea will, however, afford an easy explanation of the influence of affinity by the masses of the acting substances, as elucidated by the experiments of M. Berthollet; for the combined effect of many particles possessing a feeble electrical energy, may be conceived equal or even superior to the effect of a few particles possessing a strong electrical energy: and the facts mentioned, page 108, confirm the supposition: for concentrated alkaline lixivia resist the transmission of acids by electricity much more powerfully than weak ones.

Allowing combination to depend upon the balance of the natural electrical energies of bodies, it is easy to conceive that a *measure* may be found of the artificial energies, as to intensity and quantity produced in the common electrical machine, or the Voltaic apparatus, capable of destroying this equilibrium; and such a measure would enable us to make a scale of electrical powers corresponding to degrees of affinity.

In the circuit of the Voltaic apparatus, completed by metallic wires and water, the strength of the opposite electricities diminish from the points of contact of the wires towards the middle point in the water, which is necessarily neutral. In a body of water of considerable length it probably would not be difficult to assign the places in which the different neutral compounds yielded to, or resisted, decomposition. Sulphate of barytes, in all cases that I tried, required immediate contact with the wire: solution of sulphate of potash exhibited no marks of decomposition with the power of 150, when connected in a circuit of water ten inches in length, at four inches from the positive point; but when placed within two inches, its alkali was slowly repelled and its acid attracted*.

Whenever

* In this expriment, the water was contained in a circular glass bason two inches deep, the communication was made by pieces of amianthus of about the

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Whenever bodies brought by artificial means into a high state of opposite electricities are made to restore the equilibrium, heat and light are the common consequences. It is perhaps an additional circumstance, in favour of the theory to state, that heat and light are likewise the result of all intense chemical action. And as in certain forms of the Voltaic battery, where large quantities of electricity of low intensity act, heat is produced without light; so in slow combinations there is an increase of temperature without luminous appearance.

The effect of heat, in producing combination, may be easily explained according to these ideas. It not only often gives more freedom of motion to the particles, but in a number of cases it seems to exalt the electrical energies of bodies; glass, the tourmalin, sulphur, all afford familiar instances of this last species of energy.

I heated together an insulated plate of copper and a plate of sulphur, and examined their electricities as their temperature became elevated: these electricities, scarcely sensible at 56° Fahrenheit to the condensing electrometer, became at 100° Fahrenheit capable of affecting the gold leaves without condensation; they increased in a still higher ratio as the sulphur approached towards its point of fusion. At a little above this point, as is well known from the experiments of the Dutch chemists, the two substances rapidly combine, and heat and light are evident.

Similar effects may be conceived to occur in the case of oxygen and hydrogen, which form water, a body apparently neutral in electrical energy to most other substances; and we may reasonably conclude that there is the same exalta-

the eighth of an inch in breadth. The saline solution filled a half ounce measure, and the distance between the solution and the water, at both points of communication, was a quarter of an inch. I mention these circumstances because the quantity of fluid and the extent of surface materially influence the result in trials of this kind. Water included in glass syphons forms a much less perfect conducting chain than when diffused upon the surface of fibrous non-conducting substances of much smaller volume than the diameter of the syphons. I attempted to employ syphons in some of my first experiments; but the very great inferiority of effect as compared with that of amianthus made me altogether relinquish the use of them.

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tion of power, in all cases of combustion. In general, when the different energies are strong and in perfect equilibrium, the combination ought to be quick, the heat and light intense, and the new compound in a neutral state. This would seem to be the case in the instance just quoted; and in the circumstances of the union of the strong alkalies and acids, But where one energy is feeble, and the other strong, all the effects must be less vivid; and the compound, instead of being neutral, ought to exhibit the excess of the stronger energy.

This last idea is confirmed by all the experiments which I have been able to make on the energies of the saline compounds with regard to the metals. Nitrate and sulphate of potash, muriate of lime, oxymuriate of potash, though repeatedly touched upon a large surface by plates of copper and zinc, gave no electrical charge to them; subcarbonate of soda and borax, on the contrary, gave a slight negative charge, and alum and superphosphate of lime a feeble positive charge.

Should this principle on further inquiry be found to apply generally, the degree of the electrical energies of bodies, ascertained by means of sensible instruments, will afford new and useful indications of their composition.

IX. *On the Mode of Action on the Pile of Volta, with experimental Elucidations.*

The great tendency of the attraction of the different chemical agents, by the positive and negative surfaces in the Voltaic apparatus, seems to be to restore the electrical equilibrium. In a Voltaic battery, composed of copper, zinc, and solution of muriate of soda, all circulation of the electricity ceases, the equilibrium is restored if copper be brought in contact with the zinc on both sides: and oxygen and acids, which are attracted by the positively electrified zinc, exert similar agencies to the copper, but probably in a slighter degree, and being capable of combination with the metal, they produce a momentary equilibrium only.

The electrical energies of the metals with regard to each other, or the substances dissolved in the water, in the Voltaic

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taic and other analogous instruments, seem to be the causes that disturb the equilibrium, and the chemical changes the causes that tend to restore the equilibrium; and the phænomena most probably depend on their joint agency.

In the Voltaic pile of zinc, copper, and solution of muriate of soda, in what has been called its condition of electrical tension, the communicating plates of copper and zinc are in opposite electrical states. And with regard to electricities of such very low intensity, water is an insulating body: every copper-plate consequently produces by induction an increase of positive electricity upon the opposite zinc plate; and every zinc plate an increase of negative electricity on the opposite copper-plate: and the intensity increases with the number, and the quantity with the extent of the series.

When a communication is made between the two extreme points, the opposite electricities tend to annihilate each other; and if the fluid medium could be a substance incapable of decomposition, the equilibrium, there is every reason to believe, would be restored, and the motion of the electricity cease. But solution of muriate of soda being composed of two series of elements possessing opposite electrical energies, the oxygen and the acid are attracted by the zinc, and the hydrogen and the alkali by the copper. The balance of power is momentary only; for solution of zinc is formed, and the hydrogen disengaged. The negative energy of the copper and the positive energy of the zinc are consequently again exerted, enfeebled only by the opposing energy of the soda in contact with the copper, and the process of electromotion continues, as long as the chemical changes are capable of being carried on.

This theory in some measure reconciles the hypothetical principles of the action of the pile adopted by its illustrious inventor, with the opinions concerning the chemical origin of Galvanism, supported by the greater number of the British philosophers, and it is confirmed and strengthened by many facts and experiments.

Thus the Voltaic pile of 20 pairs of plates of copper and zinc exhibits no permanent electromotive power when the

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connecting fluid is water free from air*; for this substance does not readily undergo chemical change, and the equilibrium seems to be capable of being permanently restored through it. Concentrated sulphuric acid, which is a much more perfect conductor, is equally inefficient, for it has little action upon zinc, and is itself decomposed only by a very strong power. Piles, containing as their fluid element either pure water or sulphuric acid, will undoubtedly give single shocks, and this effect is connected with the restoration of the equilibrium disturbed by the energies of the metals; but when their extreme plates are connected there is no exhibition, as in usual cases of electromotion. Water containing loosely combined oxygen is more efficient than water containing common air, as it enables oxide of zinc to be formed more rapidly, and in larger quantities. Neutrosaline solutions which are at first very active, lose their energy in proportion as their acid arranges itself on the side of the zinc, and their alkali on that of the copper; and I have found the powers of a combination nearly destroyed from this cause very much revived, merely by agitating the fluids in the cells and mixing their parts together. Diluted acids, which are themselves easily decomposed, or which assist the decomposition of water, are above all other substances powerful; for they dissolve the zinc, and furnish only a gaseous product to the negative surface, which is immediately disengaged.

There are other experiments connected with very striking results, which offer additional reasons for supposing the decomposition of the chemical menstrua essential to the continued electromotion in the pile.

As when an electrical discharge is produced by means of small metallic surfaces in the Voltaic battery, (the opposite states being exalted,) sensible heat is the consequence, it occurred to me, that if the decomposition of the chemical agents was essential to the balance of the opposed electricities, the effect, in a saline solution, of this decomposition,

* The experiments proving this fact, and the other analogous facts in this page, may be seen detailed in Nicholson's Journal, 4to. vol. iv. page 338 and 393; and Phil. Mag. vol. x. page 40.

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and of the transfer of the alkali to the negative side, and of the acid to the positive side, ought, under favourable circumstances, to be connected with an increase of temperature.

I placed the gold cones, which have been so often mentioned, in the circuit of the battery with the power of 100, I filled them with distilled water, and connected them by a piece of moistened asbestus, about an inch in length and $\frac{1}{6}$ of an inch diameter; I provided a small air-thermometer capable of being immersed in the gold cones, expecting (if any) only a very slight change of temperature; I introduced a drop of solution of sulphate of potash into the positive cone: the decomposition instantly began: potash passed rapidly over into the negative cone, heat was immediately sensible; and in less than two minutes the water was in a state of ebullition.

I tried the same thing with a solution of nitrate of ammonia, and in this instance the heat rose to such an intensity as to evaporate all the water in three or four minutes, with a kind of explosive noise; and at last actual inflammation took place, with the decomposition and dissipation of the greatest part of the salt*.

That the increase of the conducting power of the water by the drop of saline solution had little or nothing to do with the effect, is evident from this circumstance. I introduced a quantity of strong lixivium of potash into the cones, and likewise concentrated sulphuric acid, separately, which are better conductors than solutions of the neutral salts; but there was very little sensible effect.

The same principles will apply to all the varieties of the electrical apparatus, whether containing double or single plates; and if the ideas developed in the preceding sections be correct, one property operating under different modifications is the universal cause of their activity.

* In this process ammonia was rapidly given off from the surface of the negative cone, and nitrous acid from that of the positive cone, and a white vapour was produced by their combination in the atmosphere above the apparatus.

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X. *On some general Illustrations and Applications of the foregoing Facts and Principles, and Conclusion.*

The general ideas advanced in the preceding pages are evidently directly in contradiction to the opinion advanced by Fabroni, and which, in the early stage of the investigation, appeared extremely probable, namely, that chemical changes are the primary causes of the phænomena of Galvanism.

Before the experiments of M. Volta on the electricity excited by the mere contact of metals were published, I had to a certain extent adopted this opinion; but the new facts immediately proved that another power must necessarily be concerned; for it was not possible to refer the electricity exhibited by the apposition of metallic surfaces to any chemical alterations, particularly as the effect is more distinct in a dry atmosphere, in which even the most oxidable metals do not change, than in a moist one, in which many metals undergo chemical alteration.

Other facts likewise soon occurred demonstrative of the same thing. In the Voltaic combination of diluted nitrous acid, zinc and copper, as is well known, the side of the zinc exposed to the acid is positive. But in combinations of zinc, water and diluted nitric acid, the surface exposed to the acid is negative; though if the chemical action of the acid on the zinc had been the cause of the effect, it ought to be the same in both cases.

In mere cases of chemical change likewise electricity is never exhibited. Iron burnt in oxygen gas, properly connected with a condensing electrometer, gives no charge to it during the process. Nitre and charcoal deflagrated in communication with the same instrument do not by their agencies in the slightest degree affect the gold leaves. Solid pure potash and sulphuric acid made to combine in an insulated platina crucible produce no electrical appearances. A solid amalgam of bismuth and a solid amalgam of lead become fluid when mixed together: the experiment, I find, is connected with a diminution of temperature, but with no exhibition of electrical effects. A thin plate of zinc, after being placed

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placed upon a surface of mercury, and separated by an insulating body, is found positive, the mercury is negative: the effects are exalted by heating the metals; but let them be kept in contact sufficiently long to amalgamate, and the compound gives no signs of electricity. I could mention a great number of other instances of pure chemical action in which I have used all the means in my power to ascertain the fact, and the result has been constantly the same. In cases of effervescence, indeed, particularly when accompanied by much heat, the metallic vessels employed become negative, but this is a phænomenon connected with evaporation, the change of state of a body independent of chemical change, and is to be referred to a different law*.

I mentioned the glass plates of Beccaria as affording a parallel to the case of combination in consequence of the different electrical states of bodies. In Guyton de Morveau's experiments on cohesion, the differerent metals are said to have adhered to mercury with a force proportional to their chemical affinities. But the other metals have different electrical energies, or different degrees of the same electrical energy with regard to this body; and in all cases of contact of mercury with another metal, upon a large surface, they ought to adhere in consequence of the difference of their electrical states, and that with a force proportional to the exaltation of those states. Iron, which M. Guyton found slightly adhesive, I find exhibits little positive electricity

* The change of the capacities of bodies in consequence of the alteration in their volumes or states of existence by heat, is a continually operating source of electrical effects; and, as I have hinted page 117, it often interferes with the results of experiments on the electrical energies of bodies as exhibited by contact. It is likewise probably one of the sources of the capricious results of experiments of friction, in which the same body, according as its texture is altered, or its temperature changed, assumes different states with regard to another body. Friction may be considered as a succession of contacts, and the natural energies of bodies would probably be accurately exhibited by it, if the unequal excitation of heat or its unequal communication to the different surfaces did not interfere by altering unequally their electrical capacities. Of the elements of flint glass, silex is slightly negative with regard to the metals, the soda is positive; and in contacts of glass with metals I find it exhibits the excess of the energy of the alkali: the case, as is well known, is the same in friction, the amalgam of the common machine is essential to its powerful excitation.

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after being laid upon a surface of mercury, and then separated. Tin, zinc, and copper, which adhere much more strongly, communicate higher charges to the condensing electrometer. I have had no instrument sufficiently exact to measure the differences; but it would seem that the adhesion from the difference of electrical states must have operated in these experiments*, which being proportional to the electrical energies are, on the hypothesis before stated, proportional to the chemical affinities. How far cohesion in general may be influenced or occasioned by this effect of the difference of the electrical energies of bodies, is a curious question for investigation.

Many applications of the general facts and principles to the processes of chemistry, both in art and in nature, will readily suggest themselves to the philosophical inquirer.

They offer very easy methods of separating acid and alkaline matter, when they exist in combination, either together or separately, in minerals; and the electrical powers of decomposition may be easily employed in animal and vegetable analysis.

A piece of muscular fibre, of two inches long and half an inch in diameter, after being electrified by the power of 150 for five days, became perfectly dry and hard, and left on incineration no saline matter. Potash, soda, ammonia, lime, and oxide of iron were evolved from it on the negative side, and the three common mineral acids and the phosphoric acid were given out on the positive side.

A laurel leaf treated in the same manner, appeared as if it had been exposed to a heat of 500° or 600° Fahrenheit, and was brown and parched. Green colouring matter, with resin, alkali, and lime, appeared in the negative vessel: and the positive vessel contained a clear fluid, which had the smell of peach blossoms; and which, when neutralized by potash, gave a blue-green precipitate to solution of sulphate of iron; so that it contained vegetable prussic acid.

A small plant of mint, in a state of healthy vegetation,

* Amalgamation undoubtedly must have interfered; but the general result seems to have been distinct.

was

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was made the medium of connection in the battery, its extremities being in contact with pure water; the process was carried on for 10 minutes: potash and lime were found in the negatively electrified water, and acid matter in the positively electrified water, which occasioned a precipitate in solutions of muriate of barytes, nitrate of silver, and muriate of lime. This plant recovered after the process: but a similar one, that had been electrified for four hours with like results, faded and died*. The facts show that the electrical powers of decomposition act even upon living vegetable matter; and there are some phænomena which seem to prove that they operate likewise upon living animal systems. When the fingers, after having been carefully washed with pure water, are brought in contact with this fluid in the positive part of the circuit, acid matter is rapidly developed, having the characters of a mixture of muriatic, phosphoric, and sulphuric acids: and if a similar trial be made in the negative part, fixed alkaline matter is as quickly exhibited.

The acid and alkaline tastes produced upon the tongue, in Galvanic experiments, seem to depend upon the decomposition of the saline matter contained in the living animal substance, and perhaps in the saliva.

As acid and alkaline substances are capable of being separated from their combinations in living systems by electrical powers, there is every reason to believe that by converse methods they may be likewise introduced into the animal œconomy, or made to pass through the animal organs; and the same thing may be supposed of metallic oxides; and these ideas ought to lead to some new investigations in medicine and physiology.

It is not improbable that the electrical decomposition of

* Seeds, I find, when placed in pure water in the positive part of the circuit, germinate much more rapidly than under common circumstances; but in the negative part of the circuit they do not germinate at all. Without supposing any peculiar effects from the different electricities which however may operate, the phænomenon may be accounted for from the saturation of the water near the positive metallic surface with oxygen, and of that near the negative surface with hydrogen.

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the neutral salts in different cases may admit of œconomical uses. Well burned charcoal and plumbago, or charcoal and iron, might be made the exciting powers; and such an arrangement if erected upon an extensive scale, neutrosaline matter being employed in every series, would, there is every reason to believe, produce large quantities of acids and alkalies with very little trouble or expense.

Ammonia and acids capable of decomposition, undergo chemical change in the Voltaic circuit only when they are in very concentrated solution, and in other cases are merely carried to their particular points of rest. This fact may induce us to hope that the new mode of analysis may lead us to the discovery of the true elements of bodies, if the materials acted on be employed in a certain state of concentration, and the electricity be sufficiently exalted. For if chemical union be of the nature which I have ventured to suppose, however strong the natural electrical energies of the elements of bodies may be, yet there is every probability of a limit to their strength: whereas the powers of our artificial instruments seem capable of indefinite increase.

Alterations of electrical equilibrium are continually taking place in nature; and it is probable that this influence, in its faculties of decomposition and transference, considerably interferes with the chemical alterations occurring in different parts of our system.

The electrical appearances which precede earthquakes and volcanic eruptions, and which have been described by the greater number of observers of these awful events, admit of very easy explanation on the principles that have been stated.

Besides the cases of sudden and violent change, there must be constant and tranquil alterations in which electricity is concerned, produced in various parts of the interior strata of our globe.

Where pyritous strata and strata of coal-blende occur, where the pure metals or the sulphurets are found in contact with each other, or any conducting substances, and where different strata contain different saline menstrua, electricity must be continually manifested; and it is very probable, that many

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many mineral formations have been materially influenced, or even occasioned by its agencies.

In an experiment that I made of electrifying a mixed solution of muriates of iron, of copper, of tin, and of cobalt, in a positive vessel, distilled water being in a negative vessel, all the four oxides passed along the asbestus, and into the negative tube, and a yellow metallic crust formed on the wire, and the oxides arranged themselves in a mixed state round the base of it.

In another experiment, in which carbonate of copper was diffused through water in a state of minute division, and a negative wire placed in a small perforated cube of zeolite in the water, green crystals collected round the cube; the particles not being capable of penetrating it.

By a multiplication of such instances the electrical power of transference may be easily conceived to apply to the explanation of some of the principal and most mysterious facts in geology.

And by imagining a scale of feeble powers, it would be easy to account for the association of the insoluble metallic and earthy compounds, containing acids.

Natural electricity has hitherto been little investigated, except in the case of its evident and powerful concentration in the atmosphere.

Its slow and silent operations in every part of the surface will probably be found more immediately and importantly connected with the order and œconomy of nature; and investigations on this subject can hardly fail to enlighten our philosophical systems of the earth; and may possibly place new powers within our reach.

Explanation of the Figures, Plate III.

Fig. 1, Represents the agate cups, mentioned page 5.

Fig. 2, Represents the gold cones, page 7.

Fig. 3, Represents the glass tubes, and their attached apparatus, page 105.

Fig. 4, Represents the two glass tubes, with the intermediate vessel, page 106.

In all the figures AB denote the wires, rendered one positively, the other negatively electrical; and C the connecting pieces of moistened amianthus.

XXXII. *His-*

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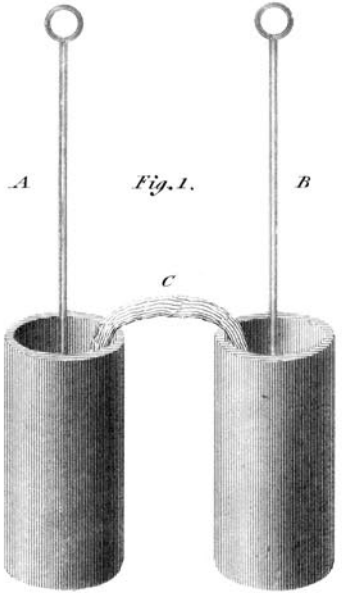

Fig. 1.

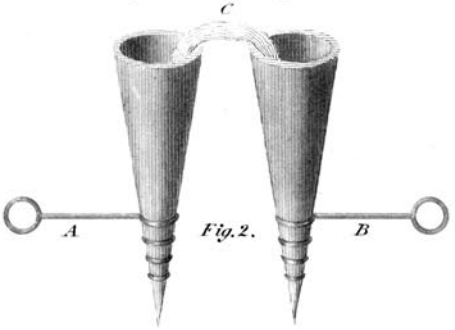

Fig. 2.

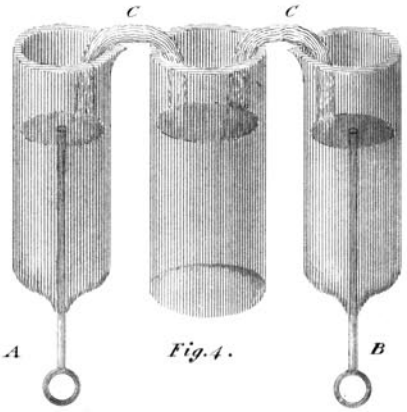

Fig. 4.

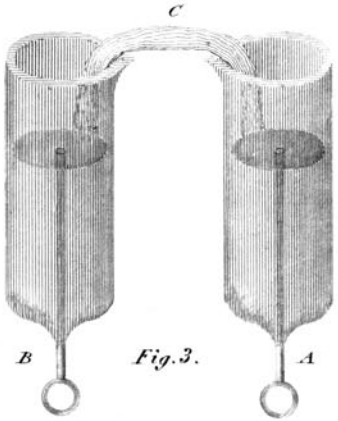

Fig. 3.