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XX. Experimental Researches in Electricity.—Eighth Series. By MICHAEL FARADAY, D.C.L. F.R.S. Fullerian Prof. Chem. Royal Institution, Corr. Memb. Royal and Imp. Acadd. of Sciences, Paris, Petersburgh, Florence, Copenhagen, Berlin, &c. &c.

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§. 14. On the Electricity of the Voltaic Pile; its source, quantity, intensity, and general characters. ¶ i. On simple Voltaic Circles. ¶ ii. On the intensity necessary for Electrolyzation. ¶ iii. On associated Voltaic Circles, or the Voltaic Battery. ¶ iv. On the resistance of an Electrolyte to Electrolytic action. ¶ v. General remarks on the active Voltaic Battery.

# ¶ i. On simple Voltaic Circles.

875. THE great question of the source of electricity in the voltaic pile has engaged the attention of so many eminent philosophers, that a man of liberal mind and able to appreciate their powers would probably conclude, although he might not have studied the question, that the truth was somewhere revealed. But if in pursuance of this impression he were induced to enter upon the work of collating results and conclusions, he would find such contradictory evidence, such equilibrium of opinion, such variation and combination of theory, as would leave him in complete doubt respecting what he should accept as the true interpretation of nature : he would be forced to take upon himself the labour of repeating and examining the facts, and then use his own judgment on them in preference to that of others.

876. This state of the subject must, to those who have made up their minds on the matter, be my apology for entering upon its investigation. The views I have taken of the definite action of electricity in decomposing bodies (783.), and the identity of the power so used with the power to be overcome (855.), founded not on a mere opinion or general notion, but on facts which, being altogether new, were to my mind precise and conclusive, gave me, as I conceived, the power of examining the question with advantages not before possessed by any, and which might compensate, on my part, for the superior clearness and extent of intellect on theirs. Such are the considerations which have induced me to suppose I might help in deciding the question, and be able to render assistance in that great service of removing *doubtful knowledge*. Such knowledge is the early morning light of every advancing science, and is essential to its development; but the man who is engaged in dispelling that which is deceptive

in it, and revealing more clearly that which is true, is as useful in his place, and as necessary to the general progress of the science, as he who first broke into the intellectual darkness, and opened a path into knowledge before unknown to man.

877. The identity of the force constituting the voltaic current or electrolytic agent, with that which holds the elements of electrolytes together (855.), or in other words with chemical affinity, seemed to indicate that the electricity of the pile itself was merely a mode of exertion, or exhibition, or existence of *true chemical action*, or rather of its cause; and I have consequently already said that I agree with those who believe that the *supply* of electricity is due to chemical powers (857.).

878. But the great question of whether it is originally due to metallic contact or to chemical action, i. e. whether it is the first or the second which *originates* and determines the current, was to me still doubtful; and the beautiful and simple experiment with amalgamated zinc and platina, which I have described minutely as to its results (863, &c.), did not decide the point; for in that experiment the chemical action does not take place without the contact of the metals, and the metallic contact is inefficient without the chemical action. Hence either might be looked upon as the *determining* cause of the current.

879. I thought it essential to decide this question by the simplest possible forms of apparatus and experiment, that no fallacy might be inadvertently admitted. The well known difficulty of effecting decomposition by a single pair of plates, except in the fluid exciting them into action (863.), seemed to throw insurmountable obstruction in the way of such experiments; but I remembered the easy decomposibility of the solution of iodide of potassium (316.), and seeing no theoretical reason, if metallic contact was not *essential*, why true electro-decomposition should not be obtained without it, even in a single circuit, I persevered and succeeded.

880. A plate of zinc, about eight inches long and half an inch wide, was cleaned and bent in the middle to a right angle, fig. 1 *a*. Plate XVIII. A plate of platina, about three inches long and half an inch wide, was fastened to a platina wire, and the latter bent as in the figure *b*. These two pieces of metal were arranged together as delineated, but as yet without the vessel *c*, and its contents, which consisted of dilute sulphuric acid mingled with a little nitric acid. At *x* a piece of folded bibulous paper, moistened in a solution of iodide of potassium, was placed on the zinc, and was pressed upon by the end of the platina wire. When under these circumstances the plates were dipped into the acid of the vessel *c*, there was an immediate effect at *x*, the iodide being decomposed, and iodine appearing at the *anode* (663.), i. e. against the end of the platina wire.

881. As long as the lower ends of the plates remained in the acid the electric current continued, and the decomposition proceeded at x. On removing the end of the wire from place to place on the paper, the effect was evidently very powerful; and on placing a piece of turmeric paper between the white paper and zinc, both papers being moistened with the solution of iodide of potassium, alkali was evolved at the



cathode (663.) against the zinc, in proportion to the evolution of iodine at the anode. Hence the decomposition was perfectly polar, and decidedly dependent upon a current of electricity passing from the zinc through the acid to the platina in the vessel c, and back from the platina through the solution to the zinc at the paper x.

882. That the decomposition at x was a true electrolytic action, due to a current determined by the state of things in the vessel c, and not dependent upon any mere direct chemical action of the zinc and platina on the iodide, or even upon any *current* which the solution of iodide might by its action on those metals tend to form at x, was shown, in the first place, by removing the vessel c and its acid from the plates, when all decomposition at x ceased, and in the next by connecting the metals, either in or out of the acid, together, when decomposition of the iodide at x occurred, but in a *reverse order*; for now alkali appeared against the end of the platina wire, and the iodine passed to the zinc, the current being the contrary of what it was in the former instance, and produced directly by the difference of action of the solution in the paper on the two metals. The iodine of course combined with the zinc.

883. When this experiment was made with pieces of zinc amalgamated over the whole surface (863.), the results were obtained with equal facility and in the same direction, even when only dilute sulphuric acid was contained in the vessel c (fig. 1.). Whichever end of the zinc was immersed in the acid, still the effects were the same : so that if, for a moment, the mercury might be supposed to supply the metallic contact, the reversion of the amalgamated piece destroys that objection. The use of unamalgamated zinc (880.) removes all possibility of doubt.

884. When, in pursuance of other views (930.), the vessel c was made to contain a solution of caustic potash in place of acid, still the same results occurred. Decomposition of the iodide was effected freely, though there was no metallic contact of dissimilar metals, and the current of electricity was in the *same direction* as when acid was used.

885. Even a solution of brine in the glass c could produce all these effects.

886. Having made a galvanometer with platina wires, and introduced it into the course of the current between the platina plate and the place of decomposition x, it was affected, giving indication of currents in the same direction as those shown to exist by the chemical action.

887. If we consider these results generally, they lead to very important conclusions. In the first place they prove, in the most decisive manner, that *metallic contact is not necessary for the production of the voltaic current*. In the next place they show a most extraordinary mutual relation of the chemical affinities of the fluid which *excites* the current, and the fluid which is *decomposed* by it.

888. For the purpose of simplifying the consideration, let us take the experiment with amalgamated zinc. The metal so prepared exhibits no effect until the current can pass: it at the same time introduces no new action, but merely removes an influence which is extraneous to those belonging either to the production or the effect of the electric current under investigation (1000.); an influence also which, when present, tends only to confuse the results.

889. Let two plates, one of amalgamated zinc and the other of platina, be placed parallel to each other (fig. 2.), and introduce a drop of dilute sulphuric acid, y, between them at one end: there will be no sensible chemical action at that spot unless the two plates are connected somewhere else, as at PZ, by a body capable of conducting electricity. If that body be a metal or certain forms of carbon, then the current passes, and, as it circulates through the fluid at y, decomposition ensues.

890. Then remove the acid from y, and introduce a drop of the solution of iodide of potassium at x (fig. 3.). Exactly the same set of effects occur, except that when the metallic communication is made at PZ, the electric current is in the opposite direction to what it was before, as is indicated by the arrows, which show the courses of the currents (667.).

891. Now both the solutions used are conductors, but the conduction in them is essentially connected with decomposition (858.) in a certain constant order, and therefore the appearance of the elements in certain places shows in what direction a current has passed when the solutions are thus employed. Moreover, we find that when they are used at opposite ends of the plates, as in the last two experiments (889. 890.), metallic contact being allowed at the other extremities, the currents are in opposite directions. We have evidently, therefore, the power of opposing the actions of the two fluids simultaneously to each other at the opposite ends of the plates, using each one as a conductor for the discharge of the current of electricity, which the other tends to generate; in fact, substituting them for metallic contact, and combining both experiments into one (fig. 4.). Under these circumstances there is an opposition of forces : the fluid, which brings into play the stronger set of chemical affinities for the zinc, (being the dilute acid,) overcomes the force of the other, and determines the formation and direction of the electric current; not merely making that current pass through the weaker liquid, but actually reversing the tendency which the elements of the latter have in relation to the zinc and platina if not thus counteracted, and forcing them in the contrary direction to that they are inclined to follow, that its own current may have free course. If the dominant action at y be removed by making metallic contact there, then the liquid at x resumes its power; or if the metals be not brought into contact at y, but the affinities of the solution there weakened, whilst those active at x are strengthened, then the latter gains the ascendancy, and the decompositions are produced in a contrary order.

892. Before drawing a *final* conclusion from this mutual dependence and state of the chemical affinities of two distant portions of acting fluids (916.), I will proceed to examine more minutely the various circumstances under which the reaction of the decomposed body is rendered evident upon the action of that body, also in the act of decomposition, which produces the voltaic current.

893. The use of metallic contact in a single pair of plates, and the cause of its great

superiority above contact made by other kinds of matter, become now very evident. When an amalgamated zinc plate is dipped into dilute sulphuric acid, the force of chemical affinity exerted between the metal and the fluid is not sufficiently powerful to cause sensible action at the surfaces of contact, and occasion the decomposition of water by the oxidation of the metal, although it *is* sufficient to produce such a condition of the electricity (or the power upon which chemical affinity depends) as would produce a current if there were a path open for it (916. 956.); and that current would complete the conditions necessary, under the circumstances, for the decomposition of the water.

894. Now the presence of a piece of platina touching both the zinc and the fluid to be decomposed, opens the path required for the electricity. Its *direct communication* with the zinc is effectual, far beyond any communication made between it and that metal, (i. e. between the platina and zinc,) by means of decomposable conducting bodies, or, in other words, *electrolytes*, as in the experiment already described (891.); because, when they are used, the chemical affinities between them and the zinc produce a contrary and opposing action to that which is influential in the dilute sulphuric acid; or if that action be but small, still the affinity of their component parts for each other has to be overcome, for they cannot conduct without suffering decomposition; and this decomposition is found *experimentally* to react back upon the forces which in the acid tend to produce the current (904. 910. &c.), and in numerous cases entirely to neutralize them. Where direct contact of the zinc and platina occurs, these obstructing forces are not brought into action, and therefore the production and the circulation of the electric current and the concomitant action of decomposition are then highly favoured.

895. It is evident, however, that one of these opposing actions may be dismissed, and yet an electrolyte be used for the purpose of completing the circuit between the zinc and platina immersed separately into the dilute acid; for if, in fig. 1, the platina wire be retained in metallic contact with the zinc plate a, at x, and a division of the platina be made elsewhere, as at s, then the solution of iodide placed there, being in contact with platina at both surfaces, exerts no chemical affinities for that metal; or if it does, they are equal on both sides. Its power, therefore, of forming a current in opposition to that dependent upon the action of the acid in the vessel c, is removed, and only its resistance to decomposition remains as the obstacle to be overcome by the affinities exerted in the dilute sulphuric acid.

896. This becomes the condition of a single pair of plates where *metallic contact* is allowed. In such cases, only one set of opposing affinities are to be overcome by those which are dominant in the vessel c; whereas, when metallic contact is not allowed, two sets of opposing affinities must be conquered (894.).

897. It has been considered a difficult, and by some an impossible, thing to decompose bodies by the current from a single pair of plates, even when it was so powerful as to heat bars of metal red hot, as in the case of HARE's calorimeter, arranged as a

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single voltaic circuit, or of WOLLASTON'S powerful single pair of metals. This difficulty has arisen altogether from the antagonism of the chemical affinity engaged in producing the current with the chemical affinity to be overcome, and depends entirely upon their relative intensity; for when the sum of forces in one has a certain degree of superiority over the sum of forces in the other, the former gains the ascendancy, determines the current, and overcomes the latter forces so as to make the substance exerting them yield up its elements in perfect accordance, both as to direction and quantity, with the course of those which are exerting the most intense action.

898. Water has generally been the substance, the decomposition of which has been sought for as a chemical test of the passage of an electric current. But I now began to perceive a reason for its failure, and for a fact which I had observed long before (315. 316.) with regard to the iodide of potassium, namely, that bodies would differ in facility of decomposition by a given electric current, according to the condition and intensity of their ordinary chemical affinities. This reason appeared in their reaction back upon the affinities tending to cause the current; and it appeared probable, that many substances might be found which could be decomposed by the current of a single pair of zinc and platina plates immersed in dilute sulphuric acid, although water resisted its action. I soon found this to be the case, and as the experiments offer new and beautiful proofs of the direct relation and opposition of the chemical affinities concerned in producing and in resisting the stream of electricity, I shall briefly describe them.

899. The arrangement of the apparatus was as in fig. 5. The vessel v contained dilute sulphuric acid; Z and P are the zinc and platina plates; a, b, and c are platina wires; the decompositions were effected at x, and occasionally, indeed generally, a galvanometer was introduced into the circuit at g: its place only is here given, the circle at g having no reference to the size of the instrument. Various arrangements were made at x, according to the kind of decomposition to be effected. If a drop of liquid was to be acted upon, the two ends were merely dipped into it; if a solution contained in the pores of paper was to be decomposed, one of the extremities was connected with a platina plate supporting the paper, whilst the other extremity rested on the paper, e, fig. 12: or sometimes, as with sulphate of soda, a plate of platina sustained two portions of paper, one of the ends of a and c resting upon each piece, c, fig. 14. The darts represent the direction of the electric current (667.).

900. Solution of *iodide of potassium*, being placed in moistened paper at the interruption of the circuit at x, was readily decomposed. Iodine was evolved at the *anode*, and alkali at the *cathode*, of the decomposing body.

901. Protochloride of tin, when fused and placed at x, was also readily decomposed, yielding perchloride of tin at the anode (779.), and tin at the cathode.

902. Fused chloride of silver, placed at x, was also easily decomposed; chlorine was evolved at the *anode*, and brilliant metallic silver, either in films upon the surface of the liquid, or in crystals beneath, evolved at the *cathode*.

903. Water acidulated with sulphuric acid, solution of muriatic acid, solution of sulphate of soda, fused nitre, and the fused chloride and iodide of lead were not decomposed by this single pair of plates, excited only by dilute sulphuric acid.

904. These experiments give abundant proofs that a single pair of plates can electrolyze bodies and separate their elements. They also show in a beautiful manner the direct relation and opposition of the chemical affinities concerned at the two points of action. In those cases where the sum of the opposing affinities at x was sufficiently beneath the sum of the acting affinities in v, decomposition took place; but in those cases where they rose higher, decomposition was effectually resisted and the current ceased to pass (891.).

905. It is, however, evident, that the sum of acting affinities in v may be increased by using other fluids than dilute sulphuric acid, in which latter case, as I believe, it is merely the affinity of the zinc for the oxygen already combined with hydrogen in the water that is exerted in producing the electric current (919.): and when the affinities are so increased, the view I am supporting leads to the conclusion, that bodies which resisted in the preceding experiments would then be decomposed, because of the increased difference between their affinities and the acting affinities thus exalted. This expectation was fully confirmed in the following manner.

906. A little nitric acid was added to the liquid in the vessel v, so as to make a mixture which I shall call diluted nitro-sulphuric acid. On repeating the experiments with this mixture, all the substances before decomposed again gave way, and much more readily. But besides that, many which before resisted electrolyzation now yielded up their elements. Thus, solution of sulphate of soda, acted upon in the interstices of litmus and turmeric paper, yielded acid at the *anode* and alkali at the *cathode*; solution of muriatic acid tinged by indigo yielded chlorine at the *cathode* and hydrogen at the *cathode*; solution of nitrate of silver yielded silver at the *cathode*. Again, fused nitre and the fused iodide and chloride of lead were decomposable by the current of this single pair of plates though they were not by the former (903.).

907. A solution of acetate of lead was apparently not decomposed by this pair, nor did water acidulated by sulphuric acid seem at first to give way (973.).

908. The increase of intensity or power of the current produced by a simple voltaic circle, with the increase of the force of the chemical action at the exciting place, is here sufficiently evident. But in order to place it in a clearer point of view, and to show that the decomposing effect was not at all dependent, in the latter cases, upon the mere capability of evolving *more* electricity, experiments were made in which the quantity evolved could be increased without variation in the intensity of the exciting cause. Thus the experiments in which dilute sulphuric acid was used (899.) were repeated, using large plates of zinc and platina in the acid; but still those bodies which resisted decomposition before, resisted it also under these new circumstances. Then again, where nitro-sulphuric acid was used (906.), mere wires of platina and zinc were immersed in the exciting acid; yet, notwithstanding this change, those

bodies were now decomposed which resisted any current tending to be formed by the dilute sulphuric acid. For instance, muriatic acid could not be decomposed by a single pair of plates when immersed in dilute sulphuric acid; nor did making the sulphuric acid strong, nor enlarging the size of the zinc and platina plates immersed in it, increase the power; but if to a weak sulphuric acid a very little nitric acid was added, then the electricity evolved had power to decompose the muriatic acid, evolving chlorine at the *anode* and hydrogen at the *cathode*, even when mere wires of metals were used. This mode of increasing the intensity of the electric current, as it excludes the effect dependent upon many pairs of plates, or even the effect of making any one acid stronger or weaker, is at once referable to the condition and force of the chemical affinities which are brought into action, and may, both in principle and practice, be considered as perfectly distinct from any other mode.

909. The direct reference which is thus experimentally made in the simple voltaic circle of the *intensity* of the electric current to the *intensity* of the chemical action going on at the place where the existence and direction of the current is determined, leads to the conclusion that by using selected bodies, as fused chlorides, salts, solutions of acids, &c., which may act upon the metals employed with different degrees of chemical force; and using also metals in association with platina, or with each other, which shall differ in the degree of chemical action exerted between them and the exciting fluid or electrolyte, we should be able to obtain a series of comparatively constant effects due to electric currents of different intensities, which would serve to assist in the construction of a scale so as to supply the means of determining relative degrees of intensity accurately in future researches.

910. I have already expressed the view which I take of the decomposition in the experimental place, as being the direct consequence of the superior exertion at some other spot of the same kind of power as that to be overcome, and therefore as the result of an antagonism of forces of the same nature (891. 904.). Those at the place of decomposition have a reaction upon, and a power over, the exerting or determining set proportionate to what is needful to overcome their own power; and hence a curious result of *resistance* offered by decompositions to the original determining force, and consequently to the current. This is well shown in the cases where such bodies as chloride of lead, iodide of lead, and water would not decompose with the current produced by a single pair of zinc and platina plates in sulphuric acid (903.), although they would with a current of higher intensity produced by stronger chemical powers. In such cases no sensible portion of the current passes (967.); the action is stopped: and I am now of opinion that in the case of the law of conduction which I described in the Fourth Series of these Researches (413.), the bodies which are electrolytes in the fluid state cease to be such in the solid form, because the attractions of the particles by which they are retained in combination and in their relative position, are then too powerful for the electric current. The particles retain their places; and as decomposition is prevented, the transmission of the electricity is prevented also; and although a battery of many plates may be used, yet if it be of that perfect kind which allows of no extraneous or indirect action (1000.), the whole of the affinities concerned in the activity of that battery are at the same time also suspended and counteracted.

911. But referring to the *resistance* of each single case of decomposition, it would appear that as these differ in force according to the affinities by which the elements in the substance tend to retain their places, they also would supply cases constituting a series of degrees by which to measure the initial intensities of simple voltaic or other currents of electricity, and which, combined with the scale of intensities determined by different degrees of *acting force* (909.), would probably include a sufficient set of differences to meet almost every important case where a reference to intensity would be required.

912. According to the experiments I have already had occasion to make, I find that the following bodies are electrolytic in the order in which I have placed them, those which are first being decomposed by the current of lowest intensity. These currents were always from a single pair of plates, and may be considered as elementary voltaic forces.

Iodide of potassium (solution).Chloride of silver (fused).Protochloride of tin (fused).Chloride of lead (fused).Iodide of lead (fused).Muriatic acid (solution).Water, acidulated with sulphuric acid.

913. It is essential that in all endeavours to obtain the relative electrolytic intensity necessary for the decomposition of different bodies, attention should be paid to the nature of the electrodes, and the other bodies present which may favour secondary actions (986.). If in electro-decomposition one of the elements separated has an affinity for the electrode, or for bodies present in the surrounding fluid, then the affinity resisting decomposition is in part balanced by such power, and the true place of the electrolyte in a table of the above kind is not obtained: thus, chlorine combines with a positive platina electrode freely, but iodine scarcely at all, and therefore I believe it is that the chloride stands first in the preceding Table. Again, if in the decomposition of water not merely sulphuric but also a little nitric acid be present, then the water is more freely decomposed, for the hydrogen at the *cathode* is not ultimately expelled, but finds oxygen in the nitric acid, with which it can combine to produce a secondary result; the affinities opposing decomposition are in this way diminished, and the elements of the water can then be separated by a current of lower intensity.

914. Advantage may be taken of this principle to interpolate more minute degrees into the scale of initial intensities already referred to (909. 911.) than is there supposed; for by combining the force of a current *constant* in its intensity, with the use

of electrodes consisting of matter, having more or less affinity for the elements evolved from the decomposing electrolyte, various intermediate degrees may be obtained.

915. Returning to the consideration of the source of electricity (878, &c.), there is another proof of the most perfect kind that metallic contact has nothing to do with the *production* of electricity in the voltaic circuit, and further, that electricity is only another mode of the exertion of chemical forces. It is, the production of the *electric spark* before any contact of metals is made, and by the exertion of *pure and unmixed chemical forces*. The experiment, which will be described further on (956.), consists in obtaining the spark upon making contact between a plate of zinc and a plate of copper plunged into dilute sulphuric acid. In order to make the arrangement as elementary as possible, mercurial surfaces were dismissed, and the contact made by a copper wire connected with the copper plate, and then brought to touch a clean part of the zinc plate. The electric spark appeared, and it must of necessity have existed and passed *before the zinc and the copper were in contact*.

916. In order to render more distinct the principles which I have been endeavouring to establish, I will restate them in their simplest form, according to my present belief. The electricity of the voltaic pile (856. note) is not dependent either in its origin or its continuance to the contact of the metals with each other (880. 915.). It is entirely due to chemical action (882.), and is proportionate in its intensity to the intensity of the affinities concerned in its production (908.); and in its quantity to the quantity of matter which has been chemically active during its evolution (869.). This definite production is again one of the strongest proofs that the electricity is of chemical origin.

917. As volta-electro-generation is a case of mere chemical action, so volta-electrodecomposition is simply a case of the preponderance of one set of chemical affinities more powerful in their nature, over another set which are less powerful; and if the instance of two opposing sets of such forces (891.) be considered, and their mutual relation and dependence borne in mind, there appears no necessity for using, in respect to such cases, any other term than chemical affinity, (though that of electricity may be very convenient,) or supposing any new agent to be concerned in producing the results; for we may consider that the powers at the two places of action are in direct communion and balanced against each other through the medium of the metals (891.), fig. 4, in a manner analogous to that in which mechanical forces are balanced against each other by the intervention of the lever (1031.).

918. All the facts show us that that power commonly called chemical affinity, can be communicated to a distance through the metals and certain forms of carbon; that the electric current is only another form of the forces of chemical affinity; that its power is in proportion to the chemical affinities producing it; that when it is deficient in force it may be helped by calling in chemical aid, the want in the former being made up by an equivalent of the latter; that, in other words, the forces termed chemical affinity and electricity are one and the same. 919. When the circumstances connected with the production of electricity in the ordinary voltaic circuit are examined and compared, it appears that the source of that agent, always meaning the electricity which circulates and completes the current in the voltaic apparatus, and gives that apparatus power and character (947. 996.), exists in the chemical action which takes place directly between the metal and the body with which it combines, and not at all in the subsequent action of the substance so produced with the acid present\*. Thus, when zinc, platina, and dilute sulphuric acid are used, it is the union of the zinc with the oxygen of the water which determines the current; and though the acid is essential to the removal of the oxide so formed, in order that another portion of zinc may act on another portion of water, it does not, by combination with that oxide, produce any sensible portion of the current of electricity which circulates; for the quantity of electricity is dependent upon the quantity of zinc oxidized, and in definite proportion to it: its intensity is in proportion to the intensity of the chemical affinity of the zinc for the oxygen under the circumstances, and is scarcely, if at all, affected by the use of either strong or weak acid (908.).

920. Again, if zinc, platina, and muriatic acid are used, the electricity appears to be dependent upon the affinity of the zinc for the chlorine, and to be circulated in exact proportion to the number of particles of zinc and chlorine which unite, being in fact an equivalent to them.

921. But in considering this oxidation, or other direct action upon the METAL itself, as the cause and source of the electric current, it is of the utmost importance to observe that the oxygen or other body must be in a peculiar condition, namely, in the state of combination; and not only so, but limited still further, to such a state of combination, and in such proportions as will constitute an electrolyte (823.). A pair of zinc and platina plates cannot be so arranged in oxygen gas as to produce a current of electricity, or act as a voltaic circle, even though the temperature may be raised so highly as to cause oxidation of the zinc far more rapidly than if the pair of plates were plunged into dilute sulphuric acid, for the oxygen is not part of an electrolyte, and cannot therefore conduct the forces onwards by decomposition, or even as metals do by itself. Or if its gaseous state embarrass the minds of some, then liquid chlorine may be taken. It does not excite a current of electricity through the two plates by combining with the zinc, for its particles cannot transfer the electricity active at the point of combination, across to the platina. It is not a conductor of itself, like the metals; nor is it an electrolyte, so as to be capable of conduction during decomposition, and hence there is simple chemical action at the spot, and no electric current +.

<sup>\*</sup> WOLLASTON, Philosophical Transactions, 1801, p. 427.

 $<sup>\</sup>uparrow$  I do not mean to affirm that no traces of electricity ever appear in such cases. What I mean is that no electricity is evolved in any way, due or related to the causes which excite voltaic electricity, or proportionate to them. That which does appear occasionally is the smallest possible fraction of that which the acting matter could produce if arranged so as to act voltaically, probably not the one hundred thousandth, or even the millionth part, and is very probably altogether different in its source.

922. It might at first be supposed that a conducting body, not electrolytic, might answer as the third substance between the zinc and the platina; and it is true that we have some such capable of exerting chemical action upon the metals. They must, however, be chosen from the metals themselves, for there are no bodies of this kind except those substances and charcoal. To decide the matter by experiment, I made the following arrangement. Melted tin was put into a glass tube bent into the form of the letter V, fig. 6, so as to fill the half of each limb, and two pieces of thick platina wire, p, w, inserted, so as to have their ends immersed some depth in the tin; the whole was then allowed to cool, and the ends p and w connected with a delicate gal-The part of the tube at x was now reheated, whilst the portion y was vanometer. retained cool. The galvanometer was immediately influenced by the thermo-electric current produced. The heat was steadily increased at x, until at last the tin and platina combined there; an effect which is known to take place with strong chemical action and high ignition; but not the slightest additional effect occurred at the galvanometer. No other deflection than that due to the thermo-electric current was observable the whole time. Hence, though a conductor, and one capable of exerting chemical action on the tin, was used, yet, not being an *electrolyte*, not the slightest effect of an electrical current could be observed (947.).

923. From this it seems apparent that the peculiar character and condition of an electrolyte is essential in one part of the voltaic circuit; and its nature being considered, good reasons appear why it and it alone should be effectual. An electrolyte is always a compound body: it can conduct, but only whilst decomposing. Its conduction depends upon its decomposition and the transmission of its particles in directions parallel to the current; and so intimate is this connexion, that if their transition be stopped, the current is stopped also; if their course be changed, its course and direction changes with them; if they proceed in one direction, it has no power to proceed in any other than a direction invariably dependent on them. The particles of an electrolytic body are all so mutually connected, are in such relation with each other through their whole extent in the direction of the current, that if the last is not disposed of, the first is not at liberty to take up its place in the new combination which the powerful affinity of the most active metal tends to produce; and then the current itself is stopped; for the dependencies of the current and the decomposition are so mutual, that whichever be originally determined, i. e. the motion of the particles or the motion of the current, the other is invariable in its concomitant production and its relation to it.

924. Consider, then, water as an electrolyte and also as an oxidizing body. The attraction of the zinc for the oxygen is greater, under the circumstances, than that of the oxygen for the hydrogen; but in combining with it, it tends to throw into circulation a current of electricity in a certain direction. This direction is consistent (as is found by innumerable experiments) with the transfer of the hydrogen from the zinc towards the platina, and the transfer in the opposite direction of fresh oxygen from

the platina towards the zinc; so that the current *can pass* in that one line, and, whilst it passes, can consist with and favour the renewal of the conditions upon the surface of the zinc, which at first determined both the combination and circulation. Hence the continuance of the action there, and the continuation of the current. It therefore appears quite as essential that there should be an electrolyte in the circuit, in order that the action may be transferred forward, in a *certain constant direction*, as that there should be an oxidizing or other body capable of acting directly on the metal; and it also appears to be essential that these two should merge into one, or that the principle directly active on the metal by chemical action should be one of the *ions* of the electrolyte used. Whether the voltaic arrangement be excited by solution of acids, or alkalies, or sulphurets, or by fused substances (476.), this principle has always hitherto, as far as I am aware, been an *anion* (943.); and I anticipate, from a consideration of the principles of electric action, that it must of necessity be one of that class of bodies.

925. If the action of the sulphuric acid used in the voltaic circuit be considered, it will be found incompetent to produce any sensible portion of the electricity of the current by its combination with the oxide formed, for this simple reason, it is deficient in a most essential condition : it forms no part of an electrolyte, nor is it in relation with any other body present in the solution which will permit of the mutual transfer of the particles and the consequent transfer of the electricity. It is true, that as the plane at which the acid is dissolving the oxide of zinc formed by the action of the water, is in contact with the metal zinc, there seems no difficulty in considering how the oxide there could communicate an electrical state, proportionate to its own chemical action on the acid, to the metal, which is a conductor without decomposition. But on the side of the acid there is no substance to complete the circuit : the water, as water, cannot conduct it, or at least only so small a proportion that it is merely an incidental and almost inappreciable effect (970.); and it cannot conduct it as an electrolyte, because an electrolyte conducts in consequence of the mutual relation and action of its particles; and neither of the elements of the water, nor even the water itself, as far as we can perceive, are *ions* with respect to the sulphuric acid (843.)\*.

926. This view of the secondary character of the sulphuric acid as an agent in the production of the voltaic current, is further confirmed by the fact, that the current generated and transmitted is directly and exactly proportional to the quantity of water decomposed and the quantity of zinc oxidized (868. 991.): and is the same as that required to decompose the same quantity of water. As, therefore, the decomposition of the water shows that the electricity has passed by its means, there remains no other electricity to be accounted for or to be referred to any action other than that of the zinc and the water on each other.

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<sup>\*</sup> It will be seen that I here agree with Sir HUMPHRY DAVY, who has experimentally supported the opinion that acids and alkalies in combining do not produce any current of electricity. Philosophical Transactions, 1826, p. 398.

927. The general case (for it includes the former one (924.),) of acids and bases, may theoretically be stated in the following manner. Let a, fig. 7. be supposed to be a dry oxyacid, and b a dry base, in contact at c, and in electric communication at their extremities by plates of platina p p, and a platina wire w. If this acid and base were fluid, and combination took place at c, with an affinity ever so vigorous, and capable of originating an electric current, the current could not circulate in any serious degree; because, according to the experimental results, neither a nor b could conduct without being decomposed, for they are either electrolytes or else insulators, under all circumstances, except to very feeble and unimportant currents (970, 986.). Now the affinities at c are not such as tend to cause the *elements* either of a or b to separate, but only such as would make the two bodies combine together as a whole ; the point of action is, therefore, insulated, the action itself local (921, 947.), and no current can be formed.

928. If the acid and base be dissolved in water, then it is possible that a small portion of the electricity due to chemical action may be conducted by the water without decomposition (966. 984.); but the quantity will be so small as to be utterly disproportionate to that due to the equivalents of chemical force; will be merely incidental; and, as it does not involve the essential principles of the voltaic pile, it forms no part of the phenomena at present under investigation\*.

929. If for the oxyacid a hydracid be substituted (927.),—as one analogous to the muriatic, for instance,—then the state of things changes altogether, and a current due to the chemical action of the acid on the base is possible. But now both the bodies act as electrolytes, for it is only one principle of each which combine mutually,—as, for instance, the chlorine with the metal,—and the hydrogen of the acid and the oxygen of the base are ready to traverse with the chlorine of the acid and the metal of the base in conformity with the current and according to the general principles already so fully laid down.

930. This view of the oxidation of the metal, or other *direct* chemical action upon it, being the sole cause of the production of the electric current in the ordinary voltaic pile, is supported by the effects which take place when alkaline or sulphuretted solutions (931. 943.) are used for the electrolytic conductor instead of dilute sulphuric acid. It was in elucidation of this point that the experiments without metallic contact, and with solution of alkali as the exciting fluid, already referred to (884.), were made.

931. Advantage was then taken of the more favourable condition offered, when metallic contact is allowed (895.), and the experiments upon the decomposition of bodies by a single pair of plates (899.) were repeated, solution of caustic potassa

<sup>\*</sup> It will, I trust, be fully understood, that in these investigations I am not professing to take an account of every small, incidental, or barely possible effect, dependent upon slight disturbances of the electric fluid during chemical action, but am seeking to distinguish and identify those actions on which the power of the voltaic battery essentially depends.

being employed in the vessel v, fig. 5. in place of dilute sulphuric acid. All the effects occurred as before: the galvanometer was deflected; the decompositions of the solutions of iodide of potassium, nitrate of silver, muriatic acid, and sulphate of soda ensued at x; and the places where the evolved principles appeared, as well as the deflection of the galvanometer, indicated a current in the *same direction* as when acid was in the vessel v; i. e. from the zinc through the solution to the platina, and back by the galvanometer and decomposing agent to the zinc.

932. The similarity in the action of either dilute sulphuric acid or potassa goes indeed far beyond this, even to the proof of identity in *quantity* as well as in *direction* of the electricity produced. If a plate of amalgamated zinc be put into a solution of potassa, it is not sensibly acted upon; but if touched in the solution by a plate of platina, hydrogen is evolved on the surface of the latter metal, and the zinc is oxidized exactly as when immersed in dilute sulphuric acid (863.). I accordingly repeated the expement before described with weighed plates of zinc (864. &c.), using however solution of potassa instead of dilute sulphuric acid. Although the time required was much longer than when acid was used, amounting to three hours for the oxidizement of 7.55 grains of zinc, still I found that the hydrogen evolved at the platina plate was the equivalent of the metal oxidized at the surface of the zinc. Hence the whole of the reasoning which was applicable in the former instance applies also here, the current being in the same direction, and its decomposing effect in the same degree, as if acid instead of alkali had been used (868.).

933. The proof, therefore, appears to me complete, that the combination of the acid with the oxide, in the former experiment, had nothing to do with the production of the electric current; for the same current is here produced when the action of the acid is absent, and the reverse action of an alkali is present. I think it cannot be supposed for a moment, that the alkali acted chemically as an acid to the oxide formed; on the contrary, our general chemical knowledge leads to the conclusion, that the ordinary metallic oxides act rather as acids to the alkalies: yet that kind of action would tend to give a reverse current in the present case, if any were due to the union of the oxide of the exciting metal with the body which combines with it. But instead of any variation of this sort, the direction of the electricity was constant, and its quantity also directly proportional to the water decomposed, or the zinc oxidized. There are reasons for believing that acids and alkalies, when in contact with metals upon which they cannot act directly, still have a power of influencing their attractions for oxygen (941.); but all the effects in these experiments prove, I think, that it is the oxidation of the metal necessarily dependent upon, and associated as it is with, the electrolyzation of the water (921. 923.), that produces the current; and that the acid or alkali merely act as solvents, and by removing the oxidized zinc, allow other portions to decompose fresh water, and so continue the evolution or determination of the current.

934. The experiments were then varied by using solution of ammonia instead of

solution of potassa; and as it, when pure, is a bad conductor, like water (554.), it was occasionally improved in that power by adding sulphate of ammonia to it. But in all the cases the effects were the same as before; decompositions of the same kind were effected, and the electric current producing these was in the same direction as in the experiments just described.

935. In order to put the equal and similar action of acid and alkali to stronger proof, arrangements were made as in fig. 8.; the glass vessel A contained dilute sulphuric acid, the corresponding glass vessel B solution of potassa, P P was a plate of platina dipping into both solutions, and ZZ two plates of amalgamated zinc connected with a delicate galvanometer. When these were plunged at the same time into the two vessels, there was generally a first feeble effect, and that in favour of the alkali, i. e. the electric current tended to pass through the vessels in the direction of the arrow, being the reverse direction of that which the acid in A would have produced alone : but the effect instantly ceased, and the action of the plates in the vessels was so equal, that, being contrary, because of the contrary position of the plates, no permanent current resulted.

936. Occasionally a zinc plate was substituted for the plate P P, and platina plates for the plates ZZ; but this caused no difference in the results: nor did a further change of the middle plate to copper produce any alteration.

937. As the opposition of electro-motive pairs of plates produces results other than those due to the mere difference of their independent actions (1011. 1045.), I devised another form of apparatus, in which the action of acid and alkali might be more directly compared. A cylindrical glass cup, about two inches deep within, an inch in internal diameter, and at least a quarter of an inch in thickness, was cut down the middle into two halves, fig. 9. A broad brass ring, larger in diameter than the cup, was supplied with a screw at one side; so that when the two halves of the cup were within the ring, and the screw was made to press tightly against the glass, the cup held any fluid put into it. Bibulous paper of 'different degrees of permeability was then cut into pieces of such a size as to be easily introduced between the loosened halves of the cup, and served when the latter were tightened again to form a porous division down the middle of the cup, sufficient to keep any two fluids on opposite sides of the paper from mingling, except very slowly, and yet allowing them to act freely as one *electrolyte*. The two spaces thus produced I will call the cells A and B, fig. 10. This instrument I have found of most general application in the investigation of the relation of fluids and metals amongst themselves and to each other. By combining its use with that of the galvanometer, it is easy to ascertain the relation of one metal with two fluids, or of two metals with one fluid, or of two metals and two fluids upon each other.

938. Dilute sulphuric acid, sp. gr. 1.25, was put into the cell A, and a strong solution of caustic potassa into the cell B; they mingled slowly through the paper, and at last a thick crust of sulphate of potassa formed on the side of the paper next to the

alkali. A plate of clean platina was put into each cell and connected with a delicate galvanometer, but no electric current could be observed. Hence the *contact* of acid with one platina plate, and alkali with the other, was unable to produce a current; nor was the combination of the acid with the alkali more effectual (925.).

939. When one of the platina plates was removed and a zinc plate substituted, either amalgamated or not, a strong electric current was produced. But, whether the zinc were in the acid whilst the platina was in the alkali, or whether the reverse order were chosen, the electric current was always from the zinc through the electrolyte to the platina, and back through the galvanometer to the zinc, the current seeming to be strongest when the zinc was in the alkali and the platina in the acid.

940. In these experiments, therefore, the acid seems to have no power over the alkali, but to be rather inferior to it in force. Hence there is no reason to suppose that the combination of the oxide formed with the acid around it has any direct influence in producing the electricity evolved, the whole of which appears to be due to the oxidation of the metal (919.).

941. The alkali, in fact, is superior to the acid in bringing a metal into what is called the positive state; for if plates of the same metal, as zinc, tin, lead, or copper, be used both in the acid or alkali, the electric current is from the alkali across the cell to the acid, and back through the galvanometer to the alkali, as Sir HUMPHRV DAVY formerly stated\*. This current is so powerful, that if amalgamated zinc, or tin, or lead be used, the metal in the acid evolves hydrogen the moment it is placed in communication with that in the alkali, not from any direct action of the acid upon it, for if the contact be broken the action ceases, but because it is powerfully negative with regard to the metal in the alkali.

942. The superiority of alkali is further proved by this, that if zinc and tin be used, or tin and lead, whichever metal is put into the alkali becomes positive, that in the acid being negative. Whichever is in the alkali is oxidized, whilst that in the acid remains in the metallic state, as far as the electric current is concerned.

943. When sulphuretted solutions are used (930.) in illustration of the assertion, that it is the chemical action of the metal and one of the *ions* of the associated electrolyte that produces all the electricity of the voltaic circuit, the proofs are still the same. Thus, as Sir HUMPHRY DAVY  $\uparrow$  has shown, if iron and copper be plunged into dilute acid, the current is from the iron through the liquid to the copper; in solution of potassa it is in the same direction, but in solution of sulphuret of potassa it is reversed. In the two first cases it is oxygen which combines with the iron, in the latter sulphur which combines with the copper, that produces the electric current; but both of these are *ions*, existing as such in the electrolyte, which is at the same moment suffering decomposition; and, what is more, both of these are *anions*, for they leave

<sup>\*</sup> Elements of Chemical Philosophy, p. 149; or Philosophical Transactions, 1826, p. 403.

<sup>†</sup> Elements of Chemical Philosophy, p. 148.

the electrolites at their *anodes*, and act just as chlorine, iodine, or any other *anion* would act which might have been previously chosen as that which should be used to throw the voltaic circle into activity.

944. The following experiments complete the series of proofs of the origin of the electricity in the voltaic pile. A fluid amalgam of potassium, containing not more than a hundredth of that metal, was put into pure water, and connected through the galvanometer with a plate of platina in the same water. There was immediately an electric current from the amalgam through the electrolyte to the platina. This must have been due to the oxidation only of the metal, for there was neither acid nor alkali to combine with, or in any way act on, the body produced. 945. Again, a plate of clean lead and a plate of platina were put into *pure* water.

945. Again, a plate of clean lead and a plate of platina were put into *pure* water. There was immediately a powerful current produced from the lead through the fluid to the platina: it was even intense enough to decompose solution of the iodide of potassium when introduced into the circuit in the form of apparatus already described (880.), fig. 1. Here no action of acid or alkali on the exide formed from the lead could supply the electricity: it was due solely to the oxidation of the metal.

946. There is no point in electrical science which seems to me of more importance than the state of the metals and the electrolytic conductor in a simple voltaic circuit *before and at* the moment when metallic contact is first completed. If clearly understood, I feel no doubt it would supply us with a direct key to the laws under which the great variety of voltaic excitements, direct and incidental, occur, and open out various new fields of research for our investigation.

947. We seem to have the power of deciding to a certain extent in numerous cases of chemical affinity, (as of zinc with the oxygen of water, &c. &c.) which of *two modes* of action of the attractive power shall be exerted (996.). In the one mode we can transfer the power onwards, and make it produce elsewhere its equivalent of action (867. 917.); in the other, it is not transferred, but exerted wholly at the spot. The first is the case of volta-electric excitation, the other ordinary chemical affinity: but both are chemical actions and due to one force or principle.

948. The general circumstances of the former mode occur in all instances of voltaic currents, but may be considered as in their perfect condition, and then free from those of the second mode, in some only of the cases; as in those of plates of zinc and platina in solution of potassa, or of amalgamated zinc and platina in dilute sulphuric acid.

in solution of potassa, or of amalgamated zinc and platina in dilute sulphuric acid. 949. Assuming it sufficiently proved, by the preceding experiments and considerations, that the electro-motive action depends, when zinc, platina, and dilute sulphuric acid are used, upon the mutual affinity of the metal zinc and the oxygen of the water (921. 924.), it would appear that the metal, when alone, has not power enough, under the circumstances, to take the oxygen and expel the hydrogen from the combination; for, in fact, no such action takes place. But it would also appear that it has power so far to act, by its attraction for the oxygen of the particles in contact with it, as to place the similar forces already active between these and the other particles of oxygen and the particles of hydrogen in the water, in a peculiar state of tension or polarity, and probably also at the same time to throw those of its own particles which are in contact with the water into a similar but opposed state. Whilst this state is retained, no further change occurs; but when it is relieved, by completion of the circuit, in which case the forces determined in opposite directions, with respect to the zinc and the electrolyte, are found exactly competent to neutralize each other, then a series of decompositions and recompositions takes place amongst the particles of oxygen and hydrogen constituting the water, between the place of relief and the place where the zinc is active; these intervening particles being evidently in close dependence upon and relation to each other. The zinc forms a direct compound with those particles of oxygen which were, immediately before, in divided relation to both it and the hydrogen : the oxide is removed by the acid, and a fresh surface of contact between the zinc and water is presented, to renew and repeat the action.

950. Practically, the state of tension is best relieved by dipping a metal which has less attraction for oxygen than the zinc, into the dilute acid, and making it also touch the zinc. The force of chemical affinity, which has been influenced or polarized in the particles of the water by the dominant attraction of the zinc for the oxygen, is then transferred, in a most extraordinary manner, through the two metals, so as to re-enter upon the circuit in the electrolytic conductor, which cannot convey or transfer it without decomposition as the metals can; or rather, probably, it is exactly balanced and neutralized by the force which at the same moment completes the combination of the zinc with the oxygen of the water. The forces, in fact, of the two particles which are acting towards each other, and which are therefore in opposite directions, are the origin of the two opposite forces, or directions of force, in the current. They are of necessity equivalent to each other. Being transferred forward in contrary directions, they produce what is called the voltaic current : and it seems to me impossible to resist the idea that it must be preceded by a *state of tension* in the fluid, and between the fluid and the zinc ; the *first consequence* of the affinity of the zinc for the oxygen of the water.

951. I have sought carefully for indications of a state of tension in the electrolytic conductor; and conceiving that it might produce something like structure, either before or during its discharge, I endeavoured to make this evident by polarized light. A glass cell, seven inches long, one inch and a half wide, and six inches deep, had two sets of platina electrodes adapted to it, one set for the ends, and the other for the sides. Those for the *sides* were seven inches long by three inches high, and when in the cell were separated by a little frame of wood covered with calico; so that when made active by connexion with a battery upon any solution in the cell, the bubbles of gas rising from them did not obscure the central parts of the liquid.

952. A saturated solution of sulphate of soda was put into the cell, and the electrodes connected with a battery of 150 pairs of 4-inch plates : the current of electricity was conducted across the cell so freely, that the discharge was as good as if a wire had been used. A ray of polarized light was then transmitted through this solution, directly across the course of the electric current, and examined by an analysing plate; but though it penetrated seven inches of solution thus subject to the action of the electricity, and though contact was sometimes made, sometimes broken, and occasionally reversed during the observations, not the slightest trace of action on the ray could be perceived.

953. The large electrodes were then removed, and others introduced which fitted the *ends* of the cell. In each a slit was cut, so as to allow the light to pass. The course of the polarized ray was now parallel to the current, or in the direction of its axis (517.); but still no effect, under any circumstances of contact or disunion, could be perceived upon it.

954. A strong solution of nitrate of lead was employed instead of the sulphate of soda, but the results were equally negative.

955. Thinking it possible that the discharge of the electric forces by the successive decompositions and recompositions of the particles of the electrolyte might neutralize and therefore destroy any effect which the first state of tension could by possibility give, I took a substance which, being an excellent electrolyte when fluid, was a perfect insulator when solid, namely, borate of lead, in the form of a glass plate, and connecting the sides and the edges of this mass with the metallic plates, sometimes in contact with the poles of a voltaic battery, and sometimes even with the electric machine, for the advantage of the much higher intensity then obtained, I passed a polarized ray across it in various directions, as before, but could not obtain the slightest appearance of action upon the light. Hence I conclude, that notwithstanding the new and extraordinary state which must be assumed by an electrolyte, either during decomposition (when a most enormous quantity of electricity must be traversing it), or in the state of tension which is assumed as preceding decomposition, and which might be supposed to be retained in the solid form of the electrolyte, still it has no power of affecting a polarized ray of light; for no kind of structure or tension can in this way be rendered evident.

956. There is, however, one beautiful experimental proof of a state of tension acquired by the metals and the electrolyte before the electric current is produced, and *before contact* of the different metals is made (915.); in fact, at that moment when chemical forces only are efficient as a cause of action. I took a voltaic apparatus, consisting of a single pair of large plates, namely, a cylinder of amalgamated zinc, and a double cylinder of copper. These were put into a jar containing dilute sulphuric acid\*, and could at pleasure be placed in metallic communication by a copper wire adjusted so as to dip at the extremities into two cups of mercury connected with the two plates.

\* When nitro-sulphuric acid is used, the spark is more powerful, but local chemical action can then commence, and proceed without requiring metallic contact. 957. Being thus arranged, there was no chemical action whilst the plates were not connected. On *making* the connexion, a spark was obtained \*, and the solution was immediately decomposed. On breaking it, the usual spark was obtained, and the decomposition ceased. In this case it is evident that the first spark must have occurred before metallic contact was made, for it passed through an interval of air, and also that it must have tended to pass before the electrolytic action began; for the latter could not take place until the current passed, and the current could not pass before the spark appeared. Hence I think there is sufficient proof, that as it is the zinc and water which by their mutual action produce the electricity of this apparatus, so these, by their first contact with each other, were placed in a state of powerful tension (951.), which, though it could not produce the actual decomposition of the water, was able to make a spark of electricity pass between the zinc and a fit discharger as soon as the interval was rendered sufficiently small. The experiment demonstrates the direct production of the electric spark from pure chemical forces.

958. There are a few circumstances connected with the production of this spark by a single pair of plates, which should be known, to ensure success to the experiment. When the amalgamated surfaces of contact are quite clean and dry, the spark, on making contact, is quite as brilliant as on breaking it, if not even more so. When a film of oxide or dirt was present at either mercurial surface, then the first spark was often feeble, and often failed, the breaking spark, however, continuing very constant and bright. When a little water was put over the mercury, the spark was greatly diminished in brilliancy, but very regular both on making and breaking contact. When the contact was made between clean platina, the spark was also very small, but regular both ways. The true electric spark is, in fact, very small, and when surfaces of mercury are used, it is the combustion of the metal which produces the greater part of the light. The circumstances connected with the burning of the mercury are most favourable on breaking contact; for the act of separation exposes clean surfaces of metal, whereas, on making contact, a thin film of oxide, or soiling matter, often interferes. Hence the origin of the general opinion that it is only when the contact is broken that the spark passes.

959. With reference to the other set of cases, namely, those in which chemical affinity is exerted (947.), but where no transference of the power to a distance takes place, and where no electric current is produced, it is evident that forces of the most intense kind must be active, and in some way balanced in their activity, during such combinations; these forces being directed so immediately and exclusively towards each other, that no signs of the powerful electric current they can produce become apparent, although the same final state of things is obtained as if that current had passed. It was BER-

\* It has been universally supposed that no spark is produced on making the contact between a single pair of plates. I was led to expect one from the considerations already advanced in this paper. The wire of communication should be short; for with a long wire, circumstances strongly affecting the spark are introduced.

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ZELIUS, I believe, who considered the heat and light evolved in cases of combustion as the consequences of this mode of exertion of the electric powers of the combining particles. But it will require a much more exact and extensive knowledge of the nature of electricity, and the manner in which it is associated with the atoms of matter, before we can understand accurately the action of this power in thus causing their union, or comprehend the nature of the great difference which it presents in the two modes of action just distinguished. We may imagine, but such imaginations must for the time be classed with the great mass of *doubtful knowledge* (876.) which we ought rather to strive to diminish than to increase; for the very extensive contradictions of this knowledge of itself shows that but a small portion of it can ultimately prove true.

960. Of the two modes of action in which chemical affinity is exerted, it is important to remark, that that which produces the electric current is as definite as that which causes ordinary chemical combination; so that in examining the production or evolution of electricity in cases of combination or decomposition, it will be necessary, not merely to observe certain effects dependent upon a current of electricity, but also their quantity: and though it may often happen that the forces concerned in any particular case of chemical action may be partly exerted in one mode and partly in the other, it is only those which are efficient in producing the current that have any relation to voltaic action. Thus, in the combination of oxygen and hydrogen to produce water, electric powers to a most enormous amount are for the time active (861. 873.); but any mode of examining the flame which they form during energetic combination, which has as yet been devised, has given but the feeblest traces. These therefore may not, cannot, be taken as evidences of the nature of the action; but are merely incidental results, incomparably small in relation to the forces concerned, and supplying no information of the way in which the particles are active on each other, or in which their forces are finally arranged.

961. That such cases of chemical action produce no *current of electricity*, is perfectly consistent with what we know of the voltaic apparatus, in which it is essential that one of the combining elements shall form part of, or be in direct relation with, an electrolytic conductor (921. 923.). That such cases produce no *free electricity of tension*, and that when they are converted into cases of voltaic action they produce a current in which the opposite forces are so equal as to neutralize each other, prove the equality of the forces in the opposed acting particles of matter, and therefore the equality of electric power in those quantities of matter which are called *electrochemical equivalents* (824.). Hence another proof of the definite nature of electrochemical action (783. &c.), and that chemical affinity and electricity are forms of the same power (917. &c.).

962. The direct reference of the effects produced by the voltaic pile at the place of experimental decomposition to the chemical affinities active at the place of excitation (891. 917.), gives a very simple and natural view of the cause why the bodies or *ions* evolved pass in certain directions; for it is only when they pass in those directions

that their forces can consist with and compensate (in direction at least) the superior forces which are dominant at the place where the action of the whole is determined. If, for instance, in a voltaic circuit, the activity of which is determined by the attraction of zinc for the oxygen of water, the zinc move from right to left, then any other *cation* included in the circuit, being part of an electrolyte, or forming part of it at the moment, will also move from right to left; and as the oxygen of the water, by its natural affinity for the zinc, moves from left to right, so any other body of the same class with it (i.e. any other *anion*), and under its government for the time, will move from left to right.

963. This I may illustrate by reference to fig. 11, the double circle of which may represent a complete voltaic circuit, the direction of its forces being determined by supposing for a moment the zinc b and the platina c as representing plates of those metals acting upon water, d, e, and other substances, but having their energy exalted so as to effect several decompositions by the use of a battery at a (989.). This supposition may be allowed, because the action in the battery will only consist of repetitions of what would take place between b and c, if they really constituted but a single pair. The zinc b, and the oxygen d, by their mutual affinity, tend to unite; but as the oxygen is already in association with the hydrogen e, and has its inherent chemical or electric powers neutralized for the time by those of the latter, the hydrogen e must leave the oxygen d, and advance in the direction of the arrow head, or else the zinc b cannot move in the same direction to unite to the oxygen d, nor the oxygen d move in the contrary direction to unite to the zinc b, the relation of the similar forces of b and e, in contrary directions, to the opposite forces of d being the preventive. As the hydrogen e advances, it, on coming against the platina c, f, which forms a part of the circuit, communicates its electric or chemical forces through it to the next electrolyte in the circuit, fused chloride of lead, g, h, where the chlorine must move in conformity with the direction of the oxygen at d, for it has to compensate the forces disturbed in its part of the circuit by the superior influence of those between the oxygen and zinc at d, b, aided as they are by those of the battery a; and for a similar reason the lead must move in the direction pointed out by the arrow head, that it may be in right relation to the first moving body of its own class, namely, the zinc b. If copper intervene in the circuit from i to k, it acts as the platina did before; and if another electrolyte, as the iodide of tin, occur at l, m, then the iodine *l*, being an *anion*, must move in conformity with the exciting *anion*, namely, the oxygen d, and the *cation* tin m move in correspondence with the other cations b, e, and h, that the chemical forces may be in equilibrium as to their direction and quantity throughout the circuit. Should it so happen that the anions in their circulation can combine with the metals at the *anodes* of the respective electrolytes, as would be the case at the platina f and the copper k, then those bodies becoming parts of electrolytes, under the influence of the current, immediately travel; but considering their relation to the zinc b, it is evidently impossible that they can travel in any other direction than what will accord with its course, and therefore can never tend to pass otherwise than *from* the anode and *to* the cathode.

964. In such a circle as that delineated, therefore, all the known *anions* may be grouped within, and all the *cations* without. If any number of them enter as *ions* into the constitution of *electrolytes*, and, forming one circuit, are simultaneously subject to one common current, the anions must move in accordance with each other in one direction, and the cations in the other. Nay, more than that, equivalent portions of these bodies must so advance in opposite directions; for the advance of every 32.5 parts of the zinc b must be accompanied by a motion in the opposite direction of 8 parts of oxygen at d, of 36 parts of chlorine at g, of 126 parts of iodine at l; and in the same direction by electro-chemical equivalents of hydrogen, lead, copper and tin, at e, h, k, and m.

965. If the present paper be accepted as a correct expression of facts, it will still only prove a confirmation of certain general views put forth by Sir HUMPHRY DAVY in his Bakerian Lecture for 1806\*, and revised and re-stated by him in another Bakerian Lecture, on electrical and chemical changes, for the year 1826 . His general statement is, that "chemical and electrical attractions were produced by the same cause, acting in one case on particles, in the other on masses, of matter; and that the same property, under different modifications, was the cause of all the phenomena exhibited by different voltaic combinations ‡." This statement I believe to be true; but in admitting and supporting it, I must guard myself from being supposed to assent to all that is associated with it in the two papers referred to, or as admitting the experiments which are there quoted as decided proofs of the truth of the principle. Had I thought them so, there would have been no occasion for this investigation. It may be supposed by some that I ought to go through these papers, distinguishing what I admit from what I reject, and giving good experimental or philosophical reasons for the judgement in both cases. But then I should be equally bound to review, for the same purpose, all that has been written both for and against the necessity of metallic contact,---for and against the origin of voltaic electricity in chemical action,—a duty which I may not undertake in the present paper  $\delta$ .

# ¶ ii. On the Intensity necessary for Electrolyzation.

966. It became requisite, for the comprehension of many of the conditions attending voltaic action, to determine positively, if possible, whether electrolytes could

\* Philosophical Transactions, 1807. † Ibid. 1826, p. 383. ‡ Ibid. 1826, p. 389. § I at one time intended to introduce here, in the form of a note, a table of reference to the papers of the different philosophers who have referred the origin of the electricity in the voltaic pile to contact, or to chemical action, or to both; but on the publication of the first volume of M. BECQUEREL's highly important and valuable Traité de l'Electricité et du Magnétism, I thought it far better to refer to that work for these references, and the views held by the authors quoted. See pages 86, 91, 104, 110, 112, 117, 118, 120, 151, 152, 224, 227, 228, 232, 233, 252, 255, 257, 258, 290, &c.—July 3rd, 1834. resist the action of an electric current if beneath a certain intensity? whether the intensity at which the current ceased to act would be the same for all bodies? and also whether the electrolytes thus resisting decomposition would conduct the electric current as a metal does, after they ceased to conduct as electrolytes, or would act as perfect insulators?

967. It was evident from the experiments described (904. 906.) that different bodies were decomposed with very different facilities, and apparently that they required for their decomposition currents of different intensities, resisting some, but giving way to others. But it was needful, by very careful and express experiments, to determine whether a current could really pass through, and yet not decompose an electrolyte (910.).

968. An arrangement (fig. 12.) was made, in which two glass vessels contained the same dilute sulphuric acid, sp. gr. 1.25. The plate z was amalgamated zinc, in connexion, by a platina wire a, with the platina plate e; b was a platina wire connecting the two platina plates PP'; c was a platina wire connected with the platina plate P''. On the plate e was placed a piece of paper moistened in solution of iodide of potassium: the wire c was so curved that its end could be made to rest at pleasure on this paper, and show, by the evolution of iodine there, whether a current was passing; or, being placed in the dotted position, it formed a direct communication with the platina plate e, and the electricity could pass without causing decomposition. The object was to produce a current by the action of the acid on the amalgamated zinc in the first vessel; to pass it through the acid in the second vessel by platina electrodes, that its power of decomposing water might, if existing, be observed; and to verify the existence of the current at pleasure, by decomposition at e, without involving the continual obstruction to the current which would arise from making the decomposition there constant. The experiment, being arranged, was examined, the existence of a current shown by the decomposition at e, and then left with the end of the wire c resting on the plate e, so as to form a constant metallic communication there.

969. After several hours, the end of the wire c was replaced on the test paper at e: decomposition occurred, and *the proof* of a passing current was therefore complete. The current was very feeble compared to what it had been at the beginning of the experiment, because of a peculiar state acquired by the metal surfaces in the second vessel, which caused them to oppose the passing current by a force which they possess under these circumstances (1040.). Still it was proved, by the decomposition, that this state of the plates in the second vessel was not able entirely to stop the current determined in the first, and that was all that was needful to be ascertained in the present inquiry.

970. This apparatus was examined from time to time, and an electric current always found circulating through it, until twelve days had elapsed, during which the water in the second vessel had been constantly subject to its action. Notwithstand-

ing this lengthened period, not the slightest appearance of a bubble upon either of the plates in that vessel occurred. From the results of the experiment, I conclude that a current *had* passed, but of so low an intensity as to fall beneath that degree at which the elements of water, unaided by any secondary force resulting from the capability of combination with the matter of the electrodes, or of the liquid surrounding them, separated from each other.

971. It may be supposed, that the oxygen and hydrogen had been evolved in such small quantities as to have entirely dissolved in the water, and finally to have escaped at the surface, or to have reunited into water. That the hydrogen can be so dissolved was shown in the first vessel; for after several days minute bubbles of gas gradually appeared upon a glass rod, inserted to retain the zinc and platina apart, and also upon the platina plate itself, and these were hydrogen. They resulted in this way. Notwithstanding the amalgamation of the zinc, the acid exerted a little direct action upon it, so that a small stream of hydrogen bubbles was continually rising from its surface; a little of this hydrogen gradually dissolved in the dilute acid, and was in part set free against the surfaces of the rod and the plate, according to the well known action of such solid bodies in solutions of gases (623. &c.).

972. But if the gases had been evolved in the second vessel by the decomposition of water, and had tended to dissolve, still there would have been every reason to expect that a few bubbles should have appeared on the electrodes, especially on the negative one, if it were only because of its action as a nucleus on the solution supposed to be formed; but none appeared even after twelve days.

973. When a few drops only of nitric acid were added to the vessel A, fig. 12., then the results were altogether different. In less than five minutes bubbles of gas appeared on the plates P' and P" in the second vessel. To prove that this was the effect of the electric current (which by trial at e was found at the same time to be passing,) the connexion at e was broken, the plates P' P" cleared from bubbles and left in the acid of the vessel B, for fifteen minutes: during that time no bubbles appeared upon them; but on restoring the communication at e, a minute did not elapse before gas appeared in bubbles upon the plates. The proof, therefore, is most full and complete, that the current excited by dilute sulphuric acid with a little nitric acid in vessel A, has intensity enough to overcome the chemical affinity exerted between the oxygen and hydrogen of the water in the vessel B, whilst that excited by dilute sulphuric acid alone has *not* sufficient intensity.

974. On using a strong solution of caustic potassa in the vessel A, to excite the current, it was found by the decomposing effects at e, that the current passed. But it had not intensity enough to decompose the water in the vessel B; for though left for fourteen days, during the whole of which time the current was found to be passing, still not the slightest appearance of gas appeared on the plates P' P", nor any other signs of the water having suffered decomposition.

975. Sulphate of soda in solution was then experimented with, for the purpose of

ascertaining with respect to it, whether a certain electrolytic intensity was also required for its decomposition in this state, in analogy with the result established with regard to water (974.). The apparatus was arranged as in fig. 13.; P and Z are the platina and zinc plates dipping into a solution of common salt; a and b are platina plates connected by wires of platina (except in the galvanometer g) with P and Z; c is a connecting wire of platina, the ends of which can be made to rest either on the plates a, b, or on the papers moistened in solutions which are placed upon them; so that the passage of the current without decomposition, or with one or two decompositions, was under ready command, as far as arrangement was concerned. In order to change the *anodes* and *cathodes* at the places of decomposition, the form of apparatus fig. 14. was occasionally adopted. Here only one platina plate, c, was used; both pieces of paper on which decomposition was to be effected were placed upon it, the wires from P and Z resting upon these pieces of paper, or upon the plate c, according as the current with or without decomposition of the solutions was required.

976. On placing solution of iodide of potassium in paper at one of the decomposing localities, and solution of sulphate of soda at the other, so that the electric current should pass through both at once, the solution of iodide was slowly decomposed, yielding iodine at the *anode* and alkali at the *cathode*; but the solution of sulphate of soda exhibited no signs of decomposition, neither acid nor alkali being evolved from it. On placing the wires so that the iodide alone was subject to the action of the current (900.), it was quickly and powerfully decomposed; but on arranging them so that the sulphate of soda alone was subject to action, it still refused to yield up its elements. Finally, the apparatus was so arranged under a wet bell-glass, that it could be left for twelve hours, the current passing during the whole time through a solution of sulphate of soda, retained in its place by only two thicknesses of bibulous litmus and turmeric paper. At the end of that time it was ascertained by the decomposition of iodide of potassium at the second place of action, that the current was passing and had passed for the twelve hours, and yet no trace of acid or alkali from the sulphate of soda appeared.

977. From these experiments it may, I think, be concluded, that a solution of sulphate of soda can conduct a current of electricity, which is unable to decompose the neutral salt present; that this salt in the state of solution, like water, requires a certain electrolytic intensity for its decomposition; and that the necessary intensity is much higher for this substance than for the iodide of potassium in a similar state of solution.

978. I then experimented on bodies rendered decomposable by fusion, and first on *chloride of lead*. The current was excited by dilute sulphuric acid without any nitric acid between zinc and platina plates, fig. 15., and was then made to traverse a little chloride of lead fused upon glass at a, a paper moistened in solution of iodide of potassium at b, and a galvanometer at g. The metallic terminations at a and b were of platina. Being thus arranged, the decomposition at b and the deflection at g

showed that an electric current was passing, but there was no appearance of decomposition at a, not even after a *metallic* communication at b was established. The experiment was repeated several times, and I am led to conclude that in this case the current has not intensity sufficient to cause the decomposition of the chloride of lead; and further, that, like water (974.), fused chloride of lead can conduct an electric current having an intensity below that required to effect decomposition.

979. Chloride of silver was then placed at a, fig. 15., instead of chloride of lead. There was a very ready decomposition of the solution of iodide of potassium at b, and when metallic contact was made there, very considerable deflection of the galvanometer needle at g. Platina also appeared to be dissolved at the anode of the fused chloride at a, and there was every appearance of a decomposition having been effected there.

980. A further proof of decomposition was obtained in the following manner. The platina wires in the fused chloride at a were brought very near together (metallic contact having been established at b), and left so; the deflection at the galvanometer indicated the passage of a current, feeble in its force, but constant. After a minute or two, however, the needle would suddenly be violently affected, and indicate a current as strong as if metallic contact had taken place at a. This I actually found to be the case, for the silver reduced by the action of the current crystallized in long delicate spiculæ, and these at last completed the metallic communication; and at the same time that they transmitted a more powerful current than the fused chloride, they proved that electro-chemical decomposition of that chloride had been going on. Hence it appears, that the current excited by dilute sulphuric acid between zinc and platina, has an intensity above that required to electrolyze the fused chloride of silver when placed between platina electrodes, although it has not intensity enough to decompose chloride of lead under the same circumstances.

981. A drop of *water* placed at a instead of the fused chlorides, showed as in the former case (970.), that it could conduct a current unable to decompose it, for decomposition of the solution of iodide at b occurred after some time. But its conducting power was much below that of the fused chloride of lead (978.).

982. Fused *nitre* at a conducted much better than water : I was unable to decide with certainty whether it was electrolyzed, but I incline to think not, for there was no discoloration against the platina at the *cathode*. If sulpho-nitric acid had been used in the exciting vessel, both the nitre and the chloride of lead would have suffered decomposition like the water (906.).

983. The results thus supplied of conduction without decomposition, and the necessity of a certain electrolytic intensity for the separation of the *ions* of different electrolytes, are immediately connected with the experiments and results given in § 10. of the Fourth Series of these Researches (418, 423, 444, 449.). But it will require a more exact knowledge of the nature of intensity, both as regards the first origin of the electric current, and also the manner in which it may be reduced, or lowered by the intervention of larger or smaller portions of bad conductors, whether decomposable or not, before their relation can be minutely and fully understood.

984. In the case of water, the experiments I have as yet made, appear to show, that, when the electric current is reduced in intensity below the point required for decomposition, then the degree of conduction is the same whether sulphuric acid, or any other of the many bodies which can affect its transferring power as an electrolyte, are present or not. Or, in other words, that the necessary electrolytic intensity for water is the same whether it be pure, or rendered a better conductor by the addition of these substances; and that for currents of less intensity than this, the water, whether pure or acidulated, has equal conducting power. An apparatus, fig. 12, was arranged with dilute sulphuric acid in the vessel A, and pure distilled water in the vessel B. By the decomposition at e, it appeared as if water was a better conductor than dilute sulphuric acid for a current of such low intensity as to cause no decomposition. I am inclined, however, to attribute this apparent superiority of water to variations in that peculiar condition of the platina electrodes which is referred to further on in this Series (1040.), and which is assumed, as far as I can judge, to a greater degree in dilute sulphuric acid than in pure water. The power, therefore, of acids, alkalies, salts, and other bodies in solution, to increase conducting power, appears to hold good only in those cases where the electrolyte subject to the current suffers decomposition, and loses all influence when the current transmitted has too low an intensity to effect chemical change. It is probable that the ordinary conducting power of an electrolyte in the solid state (419.) is the same as that which it possesses in the fluid state for currents under the due electrolytic intensity.

985. Currents of electricity, produced by less than eight or ten series of voltaic elements, can be reduced to that intensity at which water can conduct them without suffering decomposition, by causing them to pass through three or four vessels in which water shall be successively interposed between platina surfaces. The principles of interference upon which this effect depends, will be described hereafter (1009. 1018.), but the effect may be useful in obtaining currents of standard intensity, and is probably applicable to batteries of any number of pairs of plates.

986. As there appears every reason to expect that all electrolytes will be found subject to the law which requires an electric current of a certain intensity for their decomposition, but that they will differ from each other in the degree of intensity required, it will be desirable hereafter to arrange them in a table, in the order of their electrolytic intensities. Investigations on this point must, however, be very much extended, and include many more bodies than have been here mentioned before such a table can be constructed. It will be especially needful in such experiments, to describe the nature of the electrodes used, or, if possible, to select such as, like platina or plumbago in certain cases, shall have no power of assisting the separation of the *ions* to be evolved (913.).

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987. Of the two modes in which bodies can transmit the electric forces, namely, that which is so characteristically exhibited by the metals, and that in which it is accompanied by decomposition, the first appears common to all bodies, although it occurs with almost infinite degrees of difference; the second is at present distinctive of the electrolytes. It is, however, just possible that it may hereafter be extended to the metals; for their power of conducting without decomposition may, perhaps justly, be ascribed to their requiring a very high electrolytic intensity for their decomposition.

 $987\frac{1}{2}$ . The establishment of a certain electrolytic intensity being necessary before decomposition can be effected, is of great importance in all those considerations which arise regarding the probable effects of weak currents, such for instance as those produced by natural thermo-electricity, or natural voltaic arrangements. For to produce an effect of decomposition or of combination, a current must not only exist, but have a certain intensity before it can overcome the quiescent affinities opposed to it, otherwise it will be conducted, producing no permanent effects. On the other hand, the principles are also now evident by which an opposing action can be so weakened by the juxtaposition of bodies not having quite affinity enough to cause direct action between them (913.), that a very weak current shall be able to raise the sum of actions sufficiently high, and cause chemical changes to occur.

988. In concluding this division on the intensity necessary for electrolyzation, I cannot resist pointing out the following remarkable conclusion in relation to intensity generally. It would appear that when a voltaic current is produced, having a certain intensity, dependent upon the strength of the chemical affinities by which that current is excited (916.), it can decompose a particular electrolyte without relation to the quantity of electricity passed, the *intensity* deciding whether the electrolyte shall give way or not. If that conclusion be confirmed, then we may arrange circumstances so that the same quantity of electricity may pass in the same time, in at the same surface, into the same decomposing body in the same state, and yet differ in intensity, decomposing in one case and in the other not. For taking a source of too low an intensity to decompose, and ascertaining the quantity passed in a given time, it is easy to take another source having a sufficient intensity, and reducing the quantity of electricity from it by the intervention of bad conductors to the same proportion as the former current, and then all the conditions will be fulfilled to produce the result described.

## ¶ iii. On associated Voltaic circles, or the Voltaic battery.

989. Passing from the consideration of single circles (875. &c.) to their association in the voltaic battery, it is a very evident consequence, that if matters are so arranged that two sets of affinities, in place of being opposed to each other as in figg. 1, 4. (880. 891.), are made to act in conformity, then, instead of either interfering with the other, it will rather assist it. This is simply the case of two voltaic pairs of metals arranged so as to form one circuit. In such arrangements the activity of the whole is known to be increased, and when ten, or a hundred, or any larger number of such alternations are placed in conformable association with each other, the power of the whole becomes proportionably exalted, and we obtain that magnificent instrument of philosophic research, the *voltaic battery*.

990. But it is evident from the principles of definite action already laid down, that the quantity of electricity in the current cannot be increased with the increase of the quantity of metal oxidized and dissolved at each new place of chemical action.  $\mathbf{A}$ single pair of zinc and platina plates throws as much electricity into the form of a current, by the oxidation of 32.5 grains of the zinc (868.) as would be given by the same alteration of a thousand times that quantity, or nearly five pounds of metal oxidized at the surface of the zinc plates of a thousand pairs placed in regular battery order. For it is evident, that the electricity which passes across the acid from the zinc to the platina in the first cell, and which has been associated with, or even originated by, the decomposition of a definite portion of water in that cell, cannot pass from the zinc to the platina across the acid in the second cell, without the decomposition of the same quantity of water there, and the oxidation of the same quantity of zinc by it (924.949.). The same result recurs in every other cell; the electrochemical equivalent of water must be decomposed in each, before the current can pass through it; for the quantity of electricity passed, and the quantity of electrolyte decomposed, *must* be the equivalents of each other. The action in each cell, therefore, is not to increase the quantity set in motion in any one cell, but to aid in urging forward that quantity, the passing of which is consistent with the oxidation of its own zinc; and in this way it exalts that peculiar property of the current which we endeayour to express by the term *intensity*, without increasing the *quantity* beyond that which is proportionate to the quantity of zinc oxidized in any single cell of the series.

991. To prove this, I arranged ten pairs of amalgamated zinc and platina plates with dilute sulphuric acid in the form of a battery. On completing the circuit, all the pairs acted and evolved gas at the surfaces of the platina. This was collected and found to be alike in quantity for each plate; and the quantity of hydrogen evolved at any one platina plate was in the same proportion to the quantity of metal dissolved from any one zinc plate, as was given in the experiment with a single pair (864. &c.). It was therefore certain, that, just as much electricity and no more had passed through the series of ten pair of plates as had passed through, or would have been put into motion by, any single pair, notwithstanding that ten times the quantity of zinc had been consumed.

992. This truth has been proved also long ago in another way, by the action of the evolved current on a magnetic needle; the deflecting power of one pair of plates in a battery being equal to the deflecting power of the whole, provided the wires used be sufficiently large to carry the current of the single pair freely; but the *cause* 

of this equality of action could not be understood whilst the definite action and evolution of electricity (783. 869.) remained unknown.

993. The superior decomposing power of a battery over a single pair of plates is rendered evident in two ways. Electrolytes held together by an affinity so strong as to resist the action of the current from a single pair, yield up their elements to the current excited by many pairs; and that body which is decomposed by the action of one or of few pairs of metals, &c., is resolved into its *ions* the more readily as it is acted upon by electricity urged forward by many alternations.

994. Both these effects are, I think, easily understood. Whatever *intensity* may be, (and that must of course depend upon the nature of electricity, whether it consist of a fluid or fluids, or of vibrations of an ether, or any other kind or condition of matter,) there seems to be no difficulty in comprehending that the *degree* of intensity at which a current of electricity is evolved by a first voltaic element, shall be increased when that current is subjected to the action of a second voltaic element, acting in conformity and possessing equal powers with the first : and as the decompositions are merely opposed actions, but exactly of the same kind as those which generate the current (917.), it seems to be a natural consequence, that the affinity which can resist the force of a single decomposing action shall be unable to oppose the energies of many decomposing actions, operating conjointly, as in the voltaic battery.

995. That a body which can give way to a current of feeble intensity should give way more freely to one of stronger force, and yet involve no contradiction to the law of definite electrolytic action, is perfectly consistent. All the facts and also the theory I have ventured to put forth, tend to show that the act of decomposition opposes a certain force to the passage of the electric current; and that this obstruction should be overcome more or less readily, in proportion to the greater or less intensity of the decomposing current, is in perfect consistency with all our notions of the electric agent.

996. I have elsewhere (947.) distinguished the chemical action of zinc and dilute sulphuric acid into two portions; that which, acting effectually on the zinc, evolves hydrogen at once upon its surface, and that which, producing an arrangement of the chemical forces throughout the electrolyte present, (in this case water,) tends to take oxygen from it, but cannot do so unless the electric current consequent thereon can have free passage, and the hydrogen be delivered elsewhere than against the zinc. The electric current depends altogether upon the second of these; but when the current can pass, by favouring the electrolytic action it tends to diminish the former and increase the latter portion.

997. It is evident, therefore, that when ordinary zinc is used in a voltaic arrangement, there is an enormous waste of that power which it is the object to throw into the form of an electric current; a consequence which is put in its strongest point of view when it is considered that three ounces and a half of zinc, properly oxydized, can circulate enough electricity to decompose nearly one ounce of water, and cause the evolution of about 2400 cubic inches of hydrogen gas. This loss of power not only takes place during the time the electrodes of the battery are in communication, being then proportionate to the quantity of hydrogen evolved against the surface of any one of the zinc plates, but includes also *all* the chemical action which goes on when the extremities of the pile are not in communication.

998. This loss is far greater with ordinary zinc than with the pure metal, as M. DE LA RIVE has shown \*. The cause is, that when ordinary zinc is acted upon by dilute sulphuric acid, portions of copper, lead, cadmium, or other metals which it may contain, are set free upon its surface; and these, being in contact with the zinc, form small but very active voltaic circles, which cause great destruction of the zinc and evolution of hydrogen, apparently upon the zinc surface, but really upon the surface of these accidental metals. In the same proportion as they serve to discharge or convey the electricity back to the zinc, do they diminish its power of producing an electric current which shall extend to a greater distance across the acid, and be discharged only through the copper or platina plate which is associated with it for the purpose of forming a voltaic apparatus.

999. All these evils are removed by the employment of an amalgam of zinc in the manner recommended by Mr. KEMP  $\uparrow$ , or the use of the amalgamated zinc plates of Mr. STURGEON (863.), who has himself suggested and objected to their application in galvanic batteries; for he says, "Were it not on account of the brittleness and other inconveniences occasioned by the incorporation of the mercury with the zinc, amalgamation of the zinc surfaces in galvanic batteries would become an important improvement; for the metal would last much longer, and remain bright for a considerable time, even for several successive hours; essential considerations in the employment of this apparatus  $\ddagger$ ."

1000. Zinc so prepared, even though impure, does not sensibly decompose the water of dilute sulphuric acid, but still has such affinity for the oxygen, that the moment a metal which, like copper or platina, has little or no affinity, touches it in the acid, action ensues, and a powerful and abundant electric current is produced. It is probable that the mercury acts by bringing the surface, in consequence of its fluidity, into one uniform condition, and preventing those differences in character between one spot and another which are necessary for the formation of the minute voltaic circuits referred to (998.). If any difference does exist at the first moment, with regard to the proportion of zinc and mercury, at one spot on the *surface*, as compared with another, that spot having the least mercury is first acted on, and, by solution of the zinc, is soon placed in the same condition as the other parts, and the

\* Quarterly Journal of Science, 1831, p. 388; or Bibliotheque Universelle, 1830, p. 391.

† JAMESON'S Edinburgh Journal, October 1828.

<sup>‡</sup> Recent Experimental Researches, p. 42, &c. Mr. STURGEON is of course unaware of the definite production of electricity by chemical action, and is in fact quoting the experiment as the strongest argument *against* the chemical theory of galvanism.

whole plate rendered superficially uniform. One part cannot, therefore, act as a discharger to another; and hence *all* the chemical power upon the water at its surface is in that equable condition (949.), which, though it tends to produce an electric current through the liquid to another plate of metal which can act as a discharger (950.), presents no irregularities by which any one part, having weaker affinities for oxygen, can act as a discharger to another. Two excellent and important consequences follow upon this state of the metal. The first is, that the *full equivalent* of electricity is obtained for the oxidation of a certain quantity of zinc; the second, that a battery constructed with the zinc so prepared, and charged with dilute sulphuric acid, is active only whilst the electrodes are connected, and ceases to act or be acted upon by the acid the instant the communication is broken.

1001. I have had a small battery of ten pairs of plates thus constructed, and am convinced that arrangements of this kind will be very important, especially in the development and illustration of the philosophical principles of the instrument. The metals I have used are amalgamated zinc and platina, connected together by being soldered to platina wires, the whole apparatus having the form of the couronne des tasses. The liquid used was dilute sulphuric acid of sp. gr. 1.25. No action took place upon the metals except when the electrodes were in communication, and then the action upon the zinc was only in proportion to the decomposition in the experimental cell; for when the current was retarded there, it was retarded also in the battery, and no waste of the powers of the metal was incurred.

1002. In consequence of this circumstance, the acid in the cells remained active for a very much longer time than usual. In fact, time did not tend to lower it in any sensible degree; for whilst the metal was preserved to be acted upon at the proper moment, the acid also was preserved almost at its first strength. Hence a constancy of action far beyond what can be obtained with the use of common zinc.

1003. Another excellent consequence was the renewal, during the interval of rest, between two experiments of the first and most efficient state. When an amalgamated zinc and a platina plate, immersed in dilute sulphuric acid, are first connected, the current is very powerful, but instantly sinks very much in force, and in some cases actually falls to only an eighth or a tenth of that first produced (1036.). This is due to the acid which is in contact with the zinc becoming neutralized by the oxide formed; the continued quick oxidation of the metal being thus prevented. With ordinary zinc, the evolution of gas at its surface tends to mingle all the liquid together, and thus bring fresh acid against the metal, by which the oxide formed there can be removed. With the amalgamated zinc battery, at every cessation of the current, the saline solution against the zinc is gradually diffused amongst the rest of the liquid; and upon the renewal of the contact with the electrodes, the zinc plates are found most favourably circumstanced for the production of a ready and powerful current.

1004. It might at first be imagined that amalgamated zinc would be much inferior

in force to common zinc, because of the lowering of its energy, which the mercury might be supposed to occasion over the whole of its surface; but this is not the case. When the electric currents of two pairs of platina and zinc plates were opposed, the difference being that one of the zincs was amalgamated and the other not, the current from the amalgamated zinc was most powerful, although no gas was evolved against it, and much was evolved at the surface of the unamalgamated metal. Again, as DAVY has shown\*, if amalgamated and unamalgamated zinc be put in contact, and dipped into dilute sulphuric acid, or other exciting fluids, the former is positive to the latter, i.e. the current passes from the amalgamated zinc, through the fluid, to the unprepared zinc. This he accounts for by supposing that " there is not any inherent and specific property in each metal which gives it the electrical character, but that it depends upon its peculiar state—on that form of aggregation which fits it for chemical change."

1005. The superiority of the amalgamated zinc is not, however, due to any such cause, but is a very simple consequence of the state of the fluid in contact with it; for as the unprepared zinc acts directly and alone upon the fluid, whilst that which is amalgamated does not, the former (by the oxide it produces) quickly neutralizes the acid in contact with its surface, so that the progress of oxidation is retarded, whilst, at the surface of the amalgamated zinc, any oxide formed is instantly removed by the free acid present, and the clean metallic surface is always ready to act with full energy upon the water. Hence its superiority (1037.).

1006. The progress of improvement in the voltaic battery and its applications, is evidently in the contrary direction at present to what it was a few years ago; for in place of increasing the number of plates, the strength of acid, and the extent altogether of the instrument, the change is rather towards its first state of simplicity, but with a far more intimate knowledge and application of the principles which govern its force and action. Effects of decomposition can now be obtained with ten pairs of plates (417.), which required five hundred or a thousand pairs for their production in the first instance. The capability of decomposing fused chlorides, iodides, and other compounds, according to the law before established (380. &c.), and the opportunity of collecting certain of the products, without any loss, by the use of apparatus of the nature of those already described (789. 814. &c.), render it probable that the voltaic battery may become a useful and even economical manufacturing instrument; for theory evidently indicates that an equivalent of a rare substance may be obtained at the expense of three or four equivalents of a very common body, namely, zinc : and practice seems thus far to justify the expectation. In this point of view I think it very likely that plates of platina or silver may be used instead of plates of copper with advantage, and that then the evil arising occasionally from solution of the copper, and its precipitation on the zinc, (by which the electro-motive power of the zinc is so much injured,) will be avoided (1047.).

\* Philosophical Transactions, 1826, p. 405.

## ¶ iv. On the Resistance of an Electrolyte to Electrolytic Action, and on Interpositions.

1007. I have already illustrated, in the simplest possible form of experiment (891. 910.), the resistance established at the place of decomposition to the force active at the exciting place. I purpose examining the effects of this resistance more generally; but it is rather with reference to their practical interference with the action and phenomena of the voltaic battery, than with any intention at this time to offer a strict and philosophical account of their nature. Their general and principal cause is the resistance of the chemical affinities to be overcome; but there are numerous other circumstances which have a joint influence with these forces (1034. 1040. &c.), each of which would require a minute examination before a correct account of the whole could be given.

1008. As it will be convenient to describe the experiments in a form different to that in which they were made, both forms shall first be explained. Plates of platina, copper, zinc, and other metals, about three quarters of an inch wide and three inches long, were associated together in pairs by means of platina wires to which they were soldered, fig. 16, the plates of one pair being either alike or different, as might be required. These were arranged in glasses, fig. 17, so as to form Volta's crown of cups. The acid or fluid in the cups never covered the whole of any plate; and occasionally small glass rods were put into the cups, between the plates, to prevent their Single plates were used to terminate the series and complete the connexion contact. with a galvanometer, or with a decomposing apparatus (899.968. &c.), or both. Now if fig. 18 be examined and compared with fig. 19, the latter may be admitted as representing the former in its simplest condition; for the cups i, ii, and iii of the former, with their contents, are represented by the cells i, ii, and iii of the latter, and the metal plates Z and P of the former by the similar plates represented Z and P in the latter. The only difference, in fact, between the apparatus, fig. 18, and the trough represented fig. 19, is that twice the quantity of surface of contact between the metal and acid is allowed in the first to what would occur in the second.

1009. When the extreme plates of the arrangement just described, fig. 18, are connected metallically through the galvanometer g, then the whole represents a battery consisting of two pairs of zinc and platina plates urging a current forward, which has, however, to decompose water unassisted by any direct chemical affinity before it can be transmitted across the cell iii, and therefore before it can circulate. This decomposition of water, which is opposed to the passage of the current, may as a matter of convenience be considered as taking place either against the surfaces of the two platina plates which constitute the electrodes in the cell iii, or against the two surfaces of that platina plate which separates the cells ii and iii, fig. 19, from each other. It is evident that if that plate were away, the battery would consist of two pairs of plates and two cells, arranged in the most favourable position for the production of a current. The platina plate therefore, which being introduced as at x, has oxygen evolved at one

surface and hydrogen at the other (that is, if the decomposing current passes), may be considered as the cause of any obstruction arising from the decomposition of water by the electrolytic action of the current; and I have usually called it the interposed plate.

1010. In order to simplify the conditions, dilute sulphuric acid was first used in all the cells, and platina for the interposed plates; for then the initial intensity of the current which tends to be formed is constant, being due to the power which zinc has of decomposing water; and the opposing force of decomposition is also constant, the elements of the water being unassisted in their separation at the interposed plates by any affinity or secondary action at the electrodes (744.), arising either from the nature of the plate itself or the surrounding fluid.

1011. When only one voltaic pair of zinc and platina plates were used, the current of electricity was entirely stopped to all practical purposes by interposing one platina plate, fig. 20, i. e. by requiring of the current that it should decompose water, and evolve both its elements, before it should pass. This consequence is in perfect accordance with the views before given (910, 917, 973.). For as the whole result depends upon the opposition of forces at the places of electric excitement and electrodecomposition, and as water is the substance to be decomposed at both before the current can move, it is not to be expected that the zinc should have such powerful attraction for the oxygen, as not only to be able to take it from its associated hydrogen, but leave such a surplus of force as, passing to the second place of decomposition, should be there able to effect a second separation of the elements of water. Such an effect would require that the force of attraction between zinc and oxygen should under the circumstances be *at least* twice as great as the force of attraction between the oxygen and hydrogen.

1012. When two pairs of zinc and platina exciting plates were used, the current was also practically stopped by one interposed platina plate, fig. 21. There was a very feeble effect of a current at first, but it ceased almost immediately. It will be referred to, with many other similar effects, hereafter (1017.).

1013. Three pairs of zinc and platina plates, fig. 22, were able to produce a current which could pass an interposed platina plate, and effect the electrolyzation of water in cell iv. The current was evident, both by the continued deflexion of the galvanometer, and the production of bubbles of oxygen and hydrogen at the electrodes in cell iv. Hence the accumulated surplus force of these plates of zinc, which are active in decomposing water, is more than equal, when added together, to the force with which oxygen and hydrogen are combined in water, and is sufficient to cause the separation of these elements from each other.

1014. The three pairs of zinc and platina plates were now opposed by two intervening platina plates, fig. 23. In this case the current was stopped.

1015. Four pairs of zinc and platina plates were also neutralized by two interposed platina plates, fig. 24.

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1016. Five pairs of zinc and platina, with two interposed platina plates, fig. 25, gave a feeble current; there was permanent deflexion at the galvanometer, and decomposition in the cells vi and vii. But the current was very feeble; very much less than when all the intermediate plates were removed and the two extreme ones only retained; for when they were placed six inches asunder in one cell, they gave a powerful current. Hence five exciting pairs, with two interposed obstructing plates, do not give a current at all comparable to that of a single unobstructed pair.

1017. I have already said that a very feeble current passed when the series included one interposed platina and two pairs of zinc and platina plates (1012.). A similarly feeble current passed in every case, and even when only one exciting pair and four intervening platina plates were used, fig. 26, a current passed which could be detected at x, both by chemical action on the solution of iodide of potassium, and by the galvanometer. This current I believe to be due to electricity reduced in intensity below the point requisite for the decomposition of water (970. 984.); for water can conduct electricity of such low intensity by the same kind of power which it possesses in common with metals and charcoal, though it cannot conduct electricity of higher intensity without suffering decomposition, and then opposing a new force consequent thereon. With an electric current under this intensity, it is probable that increasing the number of interposed platina plates would not involve an increased difficulty of conduction.

1018. In order to obtain an idea of the additional interfering power of each added platina plate, six voltaic pairs and four intervening platinas were arranged as in fig. 27; a very feeble current then passed (985, 1017.). When one of the platinas was removed so that three intervened, a current somewhat stronger passed. With two intervening platinas a still stronger current passed; and with only one intervening platina a very fair current was obtained. But the effect of the successive plates, taken in the order of their interposition, was very different, as might be expected; for the first retarded the current more powerfully than the second, and the second more than the third.

1019. In these experiments both amalgamated and unamalgamated zinc were used, but the results generally were the same.

1020. The effects of retardation just described were altered altogether when changes were made in the *nature of the liquid* used between the plates, either in what may be called the *exciting* or the *retarding* cells. Thus, retaining the exciting force the same, by still using pure dilute sulphuric acid for that purpose, if a little nitric acid were added to the liquid in the *retarding* cells, then the transmission of the current was very much facilitated. For instance, in the experiment with one pair of exciting plates and one intervening plate (1011.), fig. 20, when a few drops of nitric acid were added to the contents of cell ii, then the current of electricity passed with considerable strength (though it soon fell from other causes (1036. 1040.),) and the same good effect was produced by the nitric acid when many interposed plates were used.

1021. This seems to be a consequence of the diminution of the difficulty of decomposing water when its hydrogen, as in these cases, instead of being absolutely expelled, is transferred to the oxygen of the nitric acid, producing a secondary result at the *cathode* (752.); for in accordance with the chemical views of the electric current and its action already advanced (913.), the water, instead of opposing a resistance to decomposition equal to the full amount of the force of mutual attraction between its oxygen and hydrogen, has that force counteracted in part, and therefore diminished by the attraction of the hydrogen at the *cathode* for the oxygen of the nitric acid which surrounds it, and with which it ultimately combines instead of being rendered in its free and independent state.

1022. When a little nitric acid was put into the exciting cells, then again the circumstances favouring the transmission of the current were strengthened, for the *intensity* of the current itself was increased by the addition (906.). When therefore a little nitric acid was added to both the *exciting* and the *retarding* cells, the current of electricity passed with very considerable freedom.

1023. When dilute muriatic acid was used, it produced and transmitted a current more easily than pure dilute sulphuric acid, but could not compete with nitric acid. As muriatic acid appears to decompose more freely than water (765.), and as the affinity of zinc for chlorine is very powerful, it might be expected to produce a current more intense than that from the use of dilute sulphuric acid; and also to transmit it more freely by undergoing decomposition at a lower intensity (912.).

1024. In relation to the effect of these interpositions, it is necessary to state that they do not appear to be at all dependent upon the size of the electrodes, or their distance from each other in the acid, except that when a current *can pass*, changes in these facilitate or retard its passage. For on repeating the experiment with one intervening and one pair of exciting plates (1011.), fig. 20, and in place of the interposed plate P using sometimes a mere wire, and sometimes very large plates (1008.), and also changing the terminal exciting plates Z and P, so that they were sometimes wires only and at others of great size, still the results were the same as those already obtained.

1025. In illustration of the effect of distance, an experiment like that described with two exciting pairs and one intervening plate (1012), fig. 21, was arranged so that the distance between the plates in the third cell could be increased to six or eight inches, or diminished to the thickness of a piece of intervening bibulous paper. Still the result was the same in both cases, the effect being no greater, sensibly, when the plates were merely separated by the paper, than when a great way apart; so that the principal opposition to the current does not depend upon the *quantity* of intervening electrolytic conductor, but on the *relation of its elements to the intensity of* the current, or to the chemical nature of the electrodes and the surrounding fluids.

1026. When the acid was sulphuric acid, *increasing its strength* in any of the cells, caused no change in the effects; it did not produce a more intense current in the

exciting cells (908.), or cause the current produced to traverse the decomposing cells more freely. But if to very weak sulphuric acid a few drops of nitric acid were added, then either one or other of those effects could be produced; and, as might be expected in a case like this, where the exciting or conducting action bore a *direct* reference to the acid itself, increasing the strength of this (the nitric acid), also increased its powers.

1027. The nature of the interposed plate was now varied to show its relation to the phenomena either of excitation or retardation, and amalgamated zinc was first substituted for platina. On employing one voltaic pair and one interposed zinc plate, fig. 28, there was as powerful a current, apparently, as if the interposed zinc plate was away. Hydrogen was evolved against P in cell ii, and against the side of the second zinc in cell i; but no gas appeared against the side of the zinc in cell ii, nor against the zinc in cell i.

1028. On interposing two amalgamated zinc plates, fig. 29, instead of one, there was still a powerful current, but interference had taken place. On using three intermediate zinc plates, fig. 30, there was still further retardation, though a good current of electricity passed.

1029. Considering the retardation as due to the inaction of the amalgamated zinc upon the dilute acid, in consequence of the slight though general effect of diminished chemical power produced by the mercury on the surface, and viewing this inaction as the circumstance which rendered it necessary that each plate should have its tendency to decompose water assisted slightly by the electric current, it was expected that plates of the metal in the unamalgamated state would probably not require such assistance, and would offer no sensible impediment to the passing of the current. This expectation was fully realized in the use of two and three interposed unamalgamated plates. The electric current passed through them as freely as if there had been no such plates in the way. They offered no obstacle, because they could decompose water without the current; and the latter had only to give direction to a part of the forces, which would have been active whether it had passed or not.

1030. Interposed plates of copper were then employed. These seemed at first to occasion no obstruction, but after a few minutes the current almost entirely ceased. This effect appears due to the surfaces taking up that peculiar condition (1040.) by which they tend to produce a reverse current; for when one or more of the plates were turned round, which could easily be effected with the couronne des tasses form of experiment, fig. 18, then the current was powerfully renewed for a few moments, and then again ceased. Plates of platina and copper, arranged as a voltaic pile with dilute sulphuric acid, could not form a voltaic trough competent to act for more than a few minutes, because of this peculiar counteracting effect.

1031. All these effects of retardation, exhibited by decomposition against surfaces for which the evolved elements have more or less affinity, or are altogether deficient in attraction, show generally, though beautifully, the chemical relations and source of the current, and also the balanced state of the affinities at the places of excitation and decomposition. In this way they add to the mass of evidence in favour of the identity of the two; for they demonstrate, as it were, the antagonism of the *chemical powers* at the electromotive part with the *chemical powers* at the interposed parts; they show that the first are *producing* electric effects, and the second *opposing* them; they bring the two into direct relation; they prove that either can determine the other, thus making what appears to be cause and effect convertible, and thereby demonstrating that both chemical and electrical action are merely two exhibitions of one single agent or power (916. &c.).

1032. It is quite evident that as water and other electrolytes can conduct electricity without suffering decomposition (986.), when the electricity is of sufficiently low intensity, it may not be asserted as absolutely true in all cases, that whenever electricity passes through an electrolyte, it produces a definite effect of decomposition. But the quantity of electricity which can pass in a given time through an electrolyte without causing decomposition, is so small as to bear no comparison to that required in a case of very moderate decomposition; and with electricity above the intensity required for decomposition, I have found no sensible departure as yet from the law of *definite electrolytic action* developed in the preceding series of these Researches (783. &c.).

1033. I cannot dismiss this division of the present Paper without making a reference to the important experiments of M. Aug. DE LA RIVE on the effects of interposed plates\*. As I have had occasion to consider such plates merely as giving rise to new decompositions, and in that way only, causing obstruction to the passage of the electric current, I was freed from the necessity of considering the peculiar effects described by that philosopher. I was the more willing to avoid for the present touching upon these, as I must at the same time have entered into the views of Sir HUMPHRY DAVY upon the same subject  $\uparrow$ , and also those of MARIANINI<sup>\*</sup> and RITTER , which are connected with it.

## ¶ v. General Remarks on the active Voltaic Battery.

1034. When the ordinary voltaic battery is brought into action, its very activity produces certain effects, which re-act upon it, and cause serious deterioration of its power. These render it an exceedingly inconstant instrument as to the *quantity* of effect which it is capable of producing. They are already, in part, known and understood; but as their importance, and that of certain other coincident results, will be more evident by reference to the principles and experiments already stated and

<sup>\*</sup> Annales de Chimie, tom. xxviii. p. 190 ; and Mémoires de Génève.

<sup>+</sup> Philosophical Transactions, 1826, p. 413.

<sup>‡</sup> Annales de Chimie, tom. xxxiii. pp. 117, 119, &c.

<sup>§</sup> Journal de Physique, tom. lvii. pp. 349, 350.

described, I have thought it would be useful, in this investigation of the voltaic pile, to notice them briefly here.

1035. When the battery is in action, it causes such substances to be formed and arrayed in contact with the plates as very much weaken its power, or even tend to produce a counter current. They are considered by Sir HUMPHRY DAVY as sufficient to account for the phenomena of RITTER's secondary piles, and also for the effects observed by M. A. DE LA RIVE with interposed platina plates\*.

1036. I have already referred to this consequence (1003.), as capable, in some cases, of lowering the force of the current to one eighth or one tenth of what it was at the first moment, and have met with instances in which its interference was very great. In an experiment in which one voltaic pair and one interposed platina plate were used with dilute sulphuric acid in the cells (fig. 31.), the wires of communication were so arranged, that the end of that marked 3 could be placed at pleasure upon paper moistened in the solution of iodide of potassium at x, or directly upon the platina plate there. If, after an interval during which the circuit had not been complete, the wire 3 were placed upon the paper, there was evidence of a current, decomposition ensued, and the galvanometer was affected. If the wire 3 were made to touch the metal of p, a comparatively strong sudden current was produced, affecting the galvanometer, but lasting only for a moment; the effect at the galvanometer ceased, and if the wire 3 were placed on the paper at x, no signs of decomposition occurred. On raising the wire 3, and breaking the circuit altogether for a while, the apparatus resumed its first power, requiring, however, from five to ten minutes for this purpose; and then, as before, on making contact between 3 and p, there was again a momentary current, and immediately all the effects apparently ceased.

1037. This effect I was ultimately able to refer to the state of the film of fluid in contact with the zinc plate in cell i. The acid of that film is instantly neutralized by the oxide formed; the oxidation of the zinc cannot, of course, go on with the same facility as before; and the chemical action being thus interrupted, the voltaic action diminishes with it. The time of the rest was required for the diffusion of the liquid, and its replacement by other acid. From the serious influence of this cause in experiments with single pairs of plates of different metals, in which I was at one time engaged, and the extreme care required to avoid it, I cannot help feeling a strong suspicion that it interferes more frequently and extensively than experimenters are aware of, and therefore direct their attention to it.

1038. In considering the effect in delicate experiments of this source of irregularity of action in the voltaic apparatus, it must be remembered that it is only that very small portion of matter which is directly in contact with the oxidizable metal which has to be considered with reference to the change of its nature; and this portion is not very readily displaced from its position upon the surface of the metal (582. 605.), especially if that

<sup>\*</sup> Philosophical Transactions, 1826, p. 413.

metal be rough and irregular. In illustration of this effect, I will quote a remarkable experiment. A burnished platina plate (569.) was put into hot strong sulphuric acid for an instant only: it was then put into distilled water, moved about in it, taken out, and wiped dry: it was put into a second portion of distilled water, moved about in it, and again wiped: it was put into a third portion of distilled water, in which it was moved about for nearly eight seconds; it was then, without wiping, put into a fourth portion of distilled water, where it was allowed to remain five minutes. The two latter portions of water were then tested for sulphuric acid; the third gave no sensible appearance of that substance, but the fourth gave indications which were not merely evident, but abundant for the circumstances under which it had been introduced. The result sufficiently shows with what difficulty that portion of the substance which is in contact with the metal leaves it; and as the contact of the fluid formed against the plate in the voltaic circuit must be as intimate and as perfect as possible, it is easy to see how quickly and greatly it must vary from the general fluid in the cells, and how influential in diminishing the force of the battery this effect must be.

1039. In the ordinary voltaic pile, the influence of this effect will occur in all variety of degrees. The extremities of a trough of twenty pairs of plates of WollAston's construction were connected with the volta-electrometer, fig. 11. (711.), of the Seventh Series of these Researches, and after five minutes the number of bubbles of gas issuing from the extremity of the tube, in consequence of the decomposition of the water, noted. Without moving the plates, the acid between the copper and zinc was agitated by the introduction of a feather. The bubbles were immediately evolved more rapidly, above twice the number being produced in the same portion of time as before. In this instance it is very evident that agitation by a feather must have been a very imperfect mode of restoring the acid in the cells against the plates towards its first equal condition; and yet imperfect as the means were, they more than doubled the power of the battery. The first effect of a battery which is known to be so superior to the action which the battery can sustain, is almost entirely due to the favourable condition of the acid in contact with the plates.

1040. A second cause of diminution in the force of the voltaic battery, consequent upon its own action, is that extraordinary state of the surfaces of the metals (969.) which was first described, I believe, by RITTER \*, to which he refers the powers of his secondary piles, and which has been so well experimented upon by MARIANINI, and also by A. DE LA RIVE. If the apparatus, fig. 31. (1036.), be left in action for an hour or two, with the wire 3 in contact with the plate p, so as to allow a free passage for the current, then, though the contact be broken for ten or twelve minutes, still, upon its renewal, only a feeble current will pass, not at all equal in force to what might be expected. Further, if P<sup>1</sup> and P<sup>2</sup> be connected by a metal wire, a powerful momentary current will pass from P<sup>2</sup> to P<sup>1</sup> through the acid, and therefore in the

\* Journal de Physique, lvii. p. 349.

reverse direction to that produced by the action of the zinc in the arrangement; and after this has happened, the general current can pass through the whole of the system as at first, but by its passage again restores the plates  $P^2$  and  $P^1$  into the former opposing condition. This, generally, is the fact described by RITTER, MARIANINI, and DE LA RIVE. It has great opposing influence on the action of a pile, especially if the latter consist of but a small number of alternations, and has to pass its current through many interpositions. It varies with the solution in which the interposed plates are immersed, with the intensity of the current, the strength of the pile, the time of action, and especially with accidental discharges of the plates by inadvertent contacts or reversions of the plates during experiments, and must be carefully watched in every endeavour to trace the source, strength, and variations of the voltaic current. Its effect was avoided in the experiments already described (1036. &c.), by making contact between the plates  $P^1$  and  $P^2$  before the effect dependent upon the state of the solution in contact with the zinc plate was observed, and by other precautions.

1041. When an apparatus like fig. 26. (1017.) with several platina plates was used, being connected with a battery able to force a current through them, the power which they acquired, of producing a reverse current, was very considerable.

1042. Weak and exhausted charges should never be used at the same time with strong and fresh ones in the different cells of a trough, or the different troughs of a battery: the fluid in all the cells should be alike, else the plates in the weaker cells, in place of assisting, retard the passage of the electricity generated in, and transmitted across, the stronger cells. Each zinc plate so circumstanced has to be assisted in decomposing power before the whole current can pass between it and the liquid. So that, if in a battery of fifty pair of plates, ten of the cells contain a weaker charge than the others, it is as if ten decomposing plates were opposed to the transit of the current of forty pairs of generating plates (1031.). Hence a serious loss of force, and hence the reason why, if the ten pairs of plates were removed, the remaining forty pairs would be much more powerful than the whole fifty.

1043. Five similar troughs, of ten pairs of plates each, were prepared, four of them with a good uniform charge of acid, and the fifth with the partially neutralized acid of a used battery. Being arranged in right order, and connected with a volta-electrometer (711.), the whole fifty pairs of plates yielded 1.1 cubic inch of oxygen and hydrogen in one minute: but on moving one of the connecting wires so that only the four well-charged troughs should be included in the circuit, they produced with the same volta-electrometer 8.4 cubical inches of gas in the same time. Nearly seven eighths of the power of the four troughs had been lost, therefore, by their association with the fifth trough.

1044. The same battery of fifty pairs of plates, after being thus used, was connected with a volta-electrometer (711.), so that by quickly shifting the wires of communication, the current of the whole of the battery, or of any portion of it, could be made to pass through the instrument for given portions of time in succession. The whole of the battery evolved 0.9 of a cubic inch of oxygen and hydrogen in half a minute; the forty plates evolved 4.6 cubic inches in the same time; the whole then evolved 1 cubic inch in the half minute; the ten weakly charged evolved 0.4 of a cubic inch in the time given: and finally the whole evolved 1.15 cubic inch in the standard time. The order of the observations was that given: the results sufficiently show the extremely injurious effect produced by the mixture of strong and weak charges in the same battery\*.

1045. In the same manner associations of *strong and weak* pairs of plates should be carefully avoided. A pair of copper and platina plates arranged in *accordance* with a pair of zinc and platina plates in dilute sulphuric acid, were found to stop the action of the latter, or even of two pairs of the latter, as effectually almost as an interposed plate of platina (1011.), or as if the copper itself had been platina. It, in fact, became an interposed decomposing plate, and therefore a retarding instead of an assisting pair.

1046. The *reversal*, by accident or otherwise, of the plates in a battery has an exceedingly injurious effect. It is not merely the counter action of the current which the reversed plates can produce, but their effect also in retarding even as indifferent plates, and requiring decomposition to be effected upon their surface, in *accordance* with the course of the current, before the latter can pass. They oppose the current, therefore, in the first place, as platina interposed plates would do (1011-1018.); and to this they add a force of opposition as counter-voltaic plates. I find that, in a series of four pair of zinc and platina plates in dilute sulphuric acid, if one pair be reversed, it very nearly neutralizes the power of the whole.

1047. There are many other causes of reaction, retardation, and irregularity in the voltaic battery. Amongst them is the not unusual one of precipitation of copper upon the zinc in the cells, the injurious effect of which has before been adverted to (1006.). But their interest is not perhaps sufficient to justify any increase of the length of this paper, which is rather intended to be an investigation of the theory of the voltaic pile than a particular account of its practical application.

Note.—Many of the views and experiments in this Series of my Experimental Researches will be seen at once to be corrections and extensions of the theory of electrochemical decomposition, given in the Fifth and Seventh Series of these Researches. The expressions I would now alter are those which relate to the independence of the evolved elements of the poles or electrodes, and the reference of their evolution to powers entirely internal (524. 537. 661.). The present paper fully shows my present views; and I would refer to paragraphs 891. 904. 910. 917. 918. 947. 963. 1007. 1031. &c., as stating what they are. I hope this note will be considered as sufficient

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<sup>\*</sup> The gradual increase in the action of the whole fifty pairs of plates was due to the elevation of temperature in the weakly charged trough by the passage of the current, in consequence of which the exciting energies of the fluid within were increased.

in the way of correction at present; for I would rather defer revising the whole theory of electro-chemical decomposition until I can obtain clearer views of the way in which the power under consideration can appear at one time as associated with particles giving them their chemical attraction, and at another as free electricity (493. 957.).—M. F.

Royal Institution, March 31, 1834.