

X. *On Voltaic Combinations. In a Letter addressed to MICHAEL FARADAY, D.C.L. F.R.S., Fullerian Prof. Chem. Royal Institution, Corr. Memb. Royal & Imp. Acadd. of Science, Paris, Petersburg, &c. By J. FREDERIC DANIELL, F.R.S., Prof. Chem. in King's College, London.*

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MY DEAR FARADAY,

YOU know how deep an interest I have taken in your “Experimental Researches in Electricity,” and how zealously I have availed myself of the opportunities, which you have ever kindly afforded me, of profiting by your oral explanation of such difficulties as occurred to me in the study of your last series of papers in the *Philosophical Transactions*. Having been early impressed with the conviction that the science of chemistry would date, from their publication, one of its great revolutions and eras of fresh impulse, I have been careful not only to store my own mind with the new facts and reasonings which they contain, but to impress them upon my pupils in my class room; and for this purpose I have been led to contrive some new apparatus and forms of experiments, by which the principles which you have promulgated have been verified, and, I think, in some instances demonstrated to advantage. In thus working in the mine which you have opened, you will be the last to be surprised if I should have moreover stumbled upon some threads of ore which you may have passed by, or temporarily abandoned, whilst following the main lode; and you will not be displeased that I venture to submit to your judgement whether there be enough of novelty or importance in the following observations to render them worthy of the attention of the Royal Society.

One result, I know, will gratify you; namely, that amongst the almost innumerable tests to which I have exposed your great discovery of the *definite chemical action of electricity*, I have found no fact to militate against it; and you will the more rejoice should I succeed in proving to you that, under the direction of this fundamental principle, I have been led to the construction of a voltaic arrangement, which furnishes a constant current of electricity for any length of time which may be required; and have thus been enabled to remove one of the greatest difficulties which have hitherto obstructed those who have endeavoured to measure and compare the different voltaic phenomena, viz. the variableness of the action of the common batteries.

You are aware of the vexatious accident by which I lost the original notes of my

experiments during the last year, which will prevent my giving you such full details of some of the results as I could have desired, although I have been careful to repeat all those in which measures are of fundamental importance.

I shall first beg to direct your attention to an arrangement which I purpose to distinguish by the name of the *Dissected Battery*; it has answered an analogous purpose to me of one of those optical instruments, by looking through which a multitude of confused lines assume a regular disposition; and many detached facts, well known before, have become clearer and of new importance, from their connexion and comparison with each other by its means. The battery consists of ten glass cells, a section of one of which is represented in the accompanying figures.

(*a, b, c, d*), Plate VIII. fig. 1. is a foot of solid glass, containing a cavity (*e, f, g, h*), the upper part of which is fitted with a stopper (*g, h*). Through this stopper the stems of the two plates (*i, j, k, l, m, n*) pass into the lower part of the cavity, which is divided into two cells by the partition (*o, p*), and each of which contains mercury, into which the wires respectively dip. This arrangement admits of the plates being changed at pleasure with little difficulty. The plates may be connected together, or with the plates of other cells, by means of wires (*p, q*) passing through the lateral holes (*t, u*) and dipping also into the cups of mercury. To the glass foot thus arranged a glass shade (*v, w, x, y, z, z*) is fitted by grinding, and constitutes a cell for the reception of the liquid. A graduated glass jar (A, B) may be suspended over either plate by means of a brass clip, proceeding from a rod placed by the side of the cell in the manner represented by fig. 2, which is a perspective drawing of a circular arrangement of ten such cells.

Fig. 3. represents the section of a cell which is adapted to the same purposes, but is less expensive in construction. It is supported in a perforated table (C, D) by its projecting rim (*v, w, y, z*), and the stems of the plates pass through the glass stopper (*a, b, c, d*) into the exterior mercury cups (*o, p*), by means of which all the necessary connexions may be made.

The active elements of the circuit which I adopted as standards of comparison were, for the metals, platinum and amalgamated zinc plates of the dimensions 3 inches by 1 inch; and for the electrolyte, water acidulated with sulphuric acid in the ratio of 100 parts by volume of the former to $2\frac{1}{4}$ of the latter (sp. gr. 1027.5), proportions which I adopted for the purpose of connecting some of my experiments with yours*.

This dilute acid was almost without local action upon the amalgamated zinc. When the plate was wholly immersed, its surface became, after some time, covered with bubbles of hydrogen gas, which strongly adhered to it; but after twenty-four hours it was found to have lost but a very small fraction of a grain of its weight. The force of heterogeneous adhesion, by which hydrogen and other gases are thus retained upon the surface of metals, I am disposed to regard as exerting a very important influence.

* Experimental Researches, x. 1127. 1128.

Fig. 2.

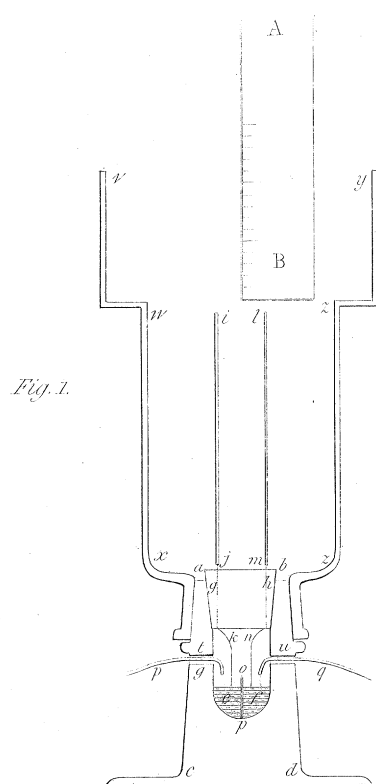
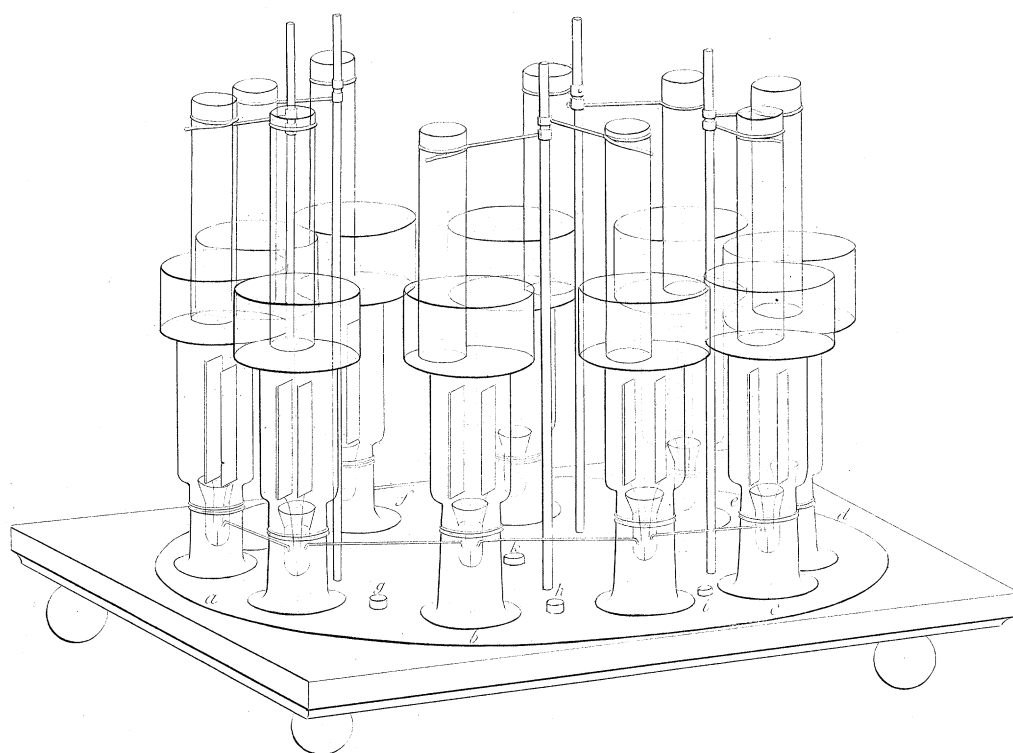


Fig. 1.

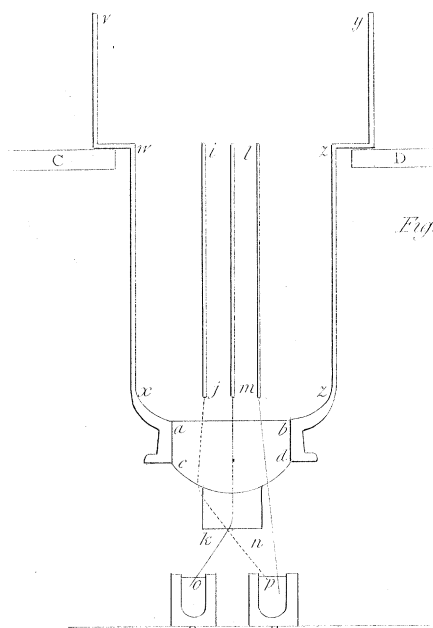


Fig. 3.

Dissected Battery.

both upon *local* and *current* affinity; and in the case before us I have little doubt that it is the affinity of the hydrogen thus tied down, as it were, to the surface of the plate which puts a stop to the decomposition of the water by the zinc. When a small quantity of nitric acid was added to the acidulated water, the same plate was entirely dissolved in a few hours without the extrication of any gaseous matter. It is probable that the elements of the nitric acid in this case acted by entering into combination with the hydrogen as it was evolved, and thus removing its opposing attraction. The decomposition also uninterruptedly proceeds when the hydrogen is evolved at a comparatively remote point in the voltaic circuit. The well-known energy of gases in what is called their *nascent state* may be referred to the same cause, namely, their adhesion to the surfaces against which they are evolved, by which their elasticity is counteracted; much in the same way, and by the same species of force, that the soluble gases are kept down by solution in water, and are enabled to exert their affinities for other forms of matter to advantage*.

Of the strength of the affinity of hydrogen in this state we have abundant evidence in the facility with which it deoxidates the oxide of copper, when sulphate of copper is exposed to it, and precipitates the metal upon the negative plate of a voltaic circuit. I shall also have occasion to prove to you in the course of this paper, that it is sufficient to deoxidate the oxide of zinc under similar circumstances; and we see at once the impossibility of the oxidation of the metal proceeding in the presence of an agent capable of abstracting oxygen from it when already combined.

When a metallic communication was made between the two plates of a cell in this its normal state, the evolution of hydrogen from the platinum was abundant, and at about the rate of three cubic inches in a quarter of an hour.

Before I proceed to describe the principal series of experiments which I instituted with this apparatus, it may perhaps be worth while to point out the facility with which, by its means, some of the principles of the voltaic battery may be demonstrated, which are the most elementary, but at the same time the most difficult to illustrate.

Taking one of the cells charged with water, acidulated with sulphuric acid, to which a small quantity of nitric acid has been added, its total inaction previous to the completion of the circuit is strongly contrasted with the torrents of gas which rise into the graduated jar placed over the platinum plate after the wires (*p*, *q*) are

* There is one well-known experiment which has given rise to much ingenious hypothesis, which may also receive its simplest explanation from the action of this force of heterogeneous adhesion, namely, the so-called metallization of ammonia. When mercury is made the negative electrode of a voltaic circuit in connexion with a strong solution of muriate of ammonia, hydrogen and ammoniacal gases are both evolved in contact with it: and not only does the adhesive force restrain the elasticity of the gases, but the latter also reacts upon the cohesion of the fluid metal, and causes it to expand and increase its volume in the manner which has been so often described. The results of the most careful examination of this amalgam by the first chemists are in entire conformity with this opinion.

brought into contact. If we take a second cell charged in the same way, and connect together the two zinc plates and the two platina, all is quiescent. No current can circulate, because the tendency of the generating plate in one cell to originate such a current in one direction of the circuit, is opposed by an equal tendency of the generating plate of the other to form one in the opposite direction. Substituting now, for the second cell, a third, charged with a solution of iodide of potassium and starch instead of the acidulated water, although it is easy to demonstrate that there is a similar tendency to form an opposing current, yet the current originating from the higher affinities of the first cell is sufficient to overcome that from the weaker affinities of the last cell, and iodine is abundantly precipitated upon the platinum plate of the latter, and immediately detected by the deep blue colour. Again, detaching the last cell, and connecting together its two plates in single circuit, its own current is established in the opposite direction, and the blue colour of the iodine speedily disappears from the platinum plate, under the influence of the hydrogen, which now takes its place. Thus your fundamental proof of the non-necessity of the contact of dissimilar metals for the establishment of an electric current is rendered very apparent and striking.

Recurring again to the two cells similarly charged with acidulated water, if instead of connecting them by their two platinum and their two zinc plates, we connect each platinum with the zinc plate of the other, the direction of the currents from both generating plates will coincide, and each, instead of opposing, will assist the other; and the completion of the circuit will be manifested by the evolution of gas in both the collecting jars.

I began my series of experiments by charging each cell with water acidulated with sulphuric acid alone, in the proportion which I have just stated; and upon connecting them in single circles I found that the amount of action of each, as measured by the quantity of hydrogen collected in their respective voltameters, in equal times, differed very materially, notwithstanding the apparent similitude of their circumstances. The difference between the highest and the lowest was nearly a third; and the inequality may probably be ascribed, partly to slight differences in the distances of the generating and conducting plates which it was not easy to avoid, and partly to differences in the amalgamated surfaces. Upon connecting them altogether in a single circular series, the inequalities disappeared: the amount of gas from each was equal, but was found to have fallen to that from the weakest cell.

The circular arrangement of the cells of the battery, fig. 2., admits of their being combined together in various ways with the greatest facility by means of small cups of mercury (*g, h, i*) placed at proper intervals. My next disposition was to connect all the platinum plates together by wires radiating from them to a central cup (*k*) of mercury, and all the zinc plates by wires dipping into a ring of the same metal placed in a groove (*a b c d e f*) surrounding the whole arrangement. In this state of things no action was of course manifest, for there was no complete circuit; but upon

making a connexion by means of a wire between the central cup and the exterior circle of mercury, the current was enabled to circulate, and was manifested by the simultaneous evolution of gas from all the cells. The inequality of action became again apparent, and the differences between the cells was nearly the same, as when they were connected in separate single circuits.

The result of this arrangement was virtually the same as that of a single pair of platinum and zinc plates, exposing the same extent of surface as that of the ten pairs added together; and the whole quantity of force generated in each cell must have passed through the single wire which connected the centre with the circumference in the progress of its circulation.

By these two arrangements of the same elements of the battery, the relations of quantity and intensity in the circulating affinity are placed in a very striking point of view. Setting aside, as we may do in our present comparison, the inequalities to which I have just referred, the same quantity of force is generated and expended in the cells in both combinations: but when in series, no connecting wire conveys more than the quantity generated in one cell to the next; whilst, in the single circuit, the whole quantity generated in all the cells must pass through the central connecting wire. This difference of quantity may be manifested by the elevation of temperature occasioned in a fine platinum wire when made the connecting medium of the latter combination, whilst the same wire will remain cold when employed for the same purpose in the former. On the other hand, the intensity of the force, though small in quantity, derived from the repeated impulses of the disposition in series, is shown by its projecting itself in the form of a spark through a break in the conductor; whilst ten times the quantity of the same force is effectually arrested in the simple circle by the slightest disruption of the continuity of its metallic path for want of this accumulated energy.

I proceeded next to combine the cells together in pairs, two platinum plates being connected, and two zinc; and the five pairs were afterwards arranged in series by wires leading from each pair of zinc to the adjoining pair of platinum. The irregularity of action again disappeared; the amount of gas was equal in all the voltameters; slightly exceeded that from the single-series arrangement; but did not quite come up to the amount of the most energetic single cell. The arrangement was equivalent to a series of five plates of double the standard size, and the quantity which circulated was determined by the least efficient pair.

Leaving one pair of cells thus connected together, the others were again disunited, and recombined with it in single series; the effect being that of a plate of double size interposed in a compound circuit with eight single. The gas collected in each of the voltameters of the double cell was exactly half of that in the several voltameters of the single cells; proving that the double plate had been reduced in efficiency to the exact standard of the single plates by its combination with them. The regulating effect of the voltaic series, by which all irregularities of its elements are equalized, is

strikingly exemplified in these experiments; and it is clearly manifest from them, as a primary law, that the circulating current must be uniform throughout its course.

In these arrangements, every cell had been a *generating* cell, and added something either to the quantity or intensity of the circulating force: I now proceeded to ascertain the effects of various *retarding* cells upon the elements of the battery. For this purpose I connected the cells together in single series, substituting a platinum plate for one of the zinc; and the obstacle reacted upon the whole series: the action was reduced by more than one third, and the quantities of gas collected from each generating cell was exactly equal to the hydrogen collected from the retarding cell. Repeating the experiment with a similar change in the next cell, the quantity of hydrogen in all the voltameters was equal, but reduced to little more than one tenth, and the current was entirely stopped by three retarding cells to seven generating cells.

When, instead of changing the zinc plate of one of the cells, I reversed its position in the series by turning the latter round, the more active opposition of the tendency in that cell to establish a contrary current was indicated by the decline of the quantity of gas in the nine voltameters of the regular cells to about one fourth; while it is remarkable that the quantity of hydrogen collected from the reversed zinc plate was considerably less. In several repetitions of this experiment this deficiency always occurred; and I also ascertained that the quantity of oxygen evolved from the corresponding platinum was the equivalent of the lesser quantity, and not of that which was evolved from the regular cells.

When one of the zinc plates was removed from the regular series, and replaced with a platinum plate which had been previously coated, by voltaic influence, with metallic copper, the phenomena were striking and instructive. No gas at first was evolved from the coppered plate, but it became slowly oxidated, and the progress of the oxidation could be traced by the gradual blackening of its surface. The oxide again was gradually dissolved, and the bright white surface of the platinum made its appearance, and oxygen gas began to be disengaged. At that moment the current received a check, which was quite appreciable by the voltameters.

As the progress of my experiments would require the use of an independent voltmeter, I thought it desirable previously to determine its retarding power by comparison with that of a single retarding cell; and for this purpose I substituted one of your upright construction for one of the cells of the battery in single series: and I found, that notwithstanding its plates were only three inches long by six eighths broad, their nearer approximation counterbalanced their deficiency of surface; and the quantity of hydrogen which the instrument indicated was exactly equal to that in the voltameters of the retarding cell. The measure of the effects of different degrees of approximation in the plates of voltaic combinations was one of the objects of my experiments; but this I have for the present postponed, for reasons which will soon be apparent.

The next variation of the standard elements of the battery was to place conducting plates in connexion with one another on each side of the generating plates. This was easily effected by making both the plates, *ij*, *lm*, (fig. 3.) of platinum communicate with one mercury cup (*p*); while the amalgamated zinc plate placed between them communicated with the other cup (*o*). This arrangement was perfectly analogous in principle to the double or WOLLASTON plates of the common battery. Upon combining the cells thus arranged in single series, nearly as much gas was collected from each plate, on the opposite sides of the generating plates, as had been collected in an equal time from the single plates; the double surface of the platinum having enabled the single zinc plate to decompose very nearly a double portion of water.

During this experiment, and its frequent repetitions, I remarked that the bubbles of hydrogen arose not only from the surfaces of the platinum which were immediately opposed to the zinc, but from the opposite surfaces likewise; and when a little sulphate of copper was added to the liquid in the cells, both faces of the plates became coated with the reduced metal.

Almost the only serious difficulty with regard to your chemical theory of voltaic action which ever occurred to me, has arisen from the well-known case of voltaic protection, in which a small piece of zinc or iron has been found to defend from corrosion a surface of copper so many hundred times its own superficial dimensions. I was unable for a long time to understand how the hydrogen, which could only be the equivalent of the oxygen taken up by the former metals, became spread over so disproportionate a surface; and this effect seemed to me more intelligible upon the hypothesis of some condition of the copper, analogous to those produced by electrical or magnetic induction, than upon any known chemical principles. The following means of determining the question by experiment now occurred to me.

I took a silver plate, fifteen inches square, and, placing it in a shallow trough, covered it with the dilute sulphuric acid, to which a portion of sulphate of copper had been added. I then supported an amalgamated zinc wire of about one eighth of an inch in diameter, so as to allow one of its ends just to rest upon the centre of the plate. The instant the two metals came in contact, a circular spot of metallic copper was thrown down upon the silver, and rapidly spread itself in such a way that in a few hours it formed a well-defined circle of six inches in diameter. Particles of copper could be traced even beyond this; but none appeared to have reached the edges of the plate.

I varied this experiment by soldering to the centre of a silver plate, 8 inches by $5\frac{1}{2}$ inches, a small piece of amalgamated zinc $\frac{7}{8}$ ths of an inch long by $\frac{3}{16}$ ths wide, and placed it perpendicularly in a jar, and covered it with the solution of copper in acidulated water. The copper immediately began to precipitate itself upon the silver, in the form of an oval surrounding the zinc, and gradually extended itself equally on all sides. There was no extension of the copper on the upper side, to indicate that the hydrogen, the reducing agent, had been carried upwards by its levity; but it spread

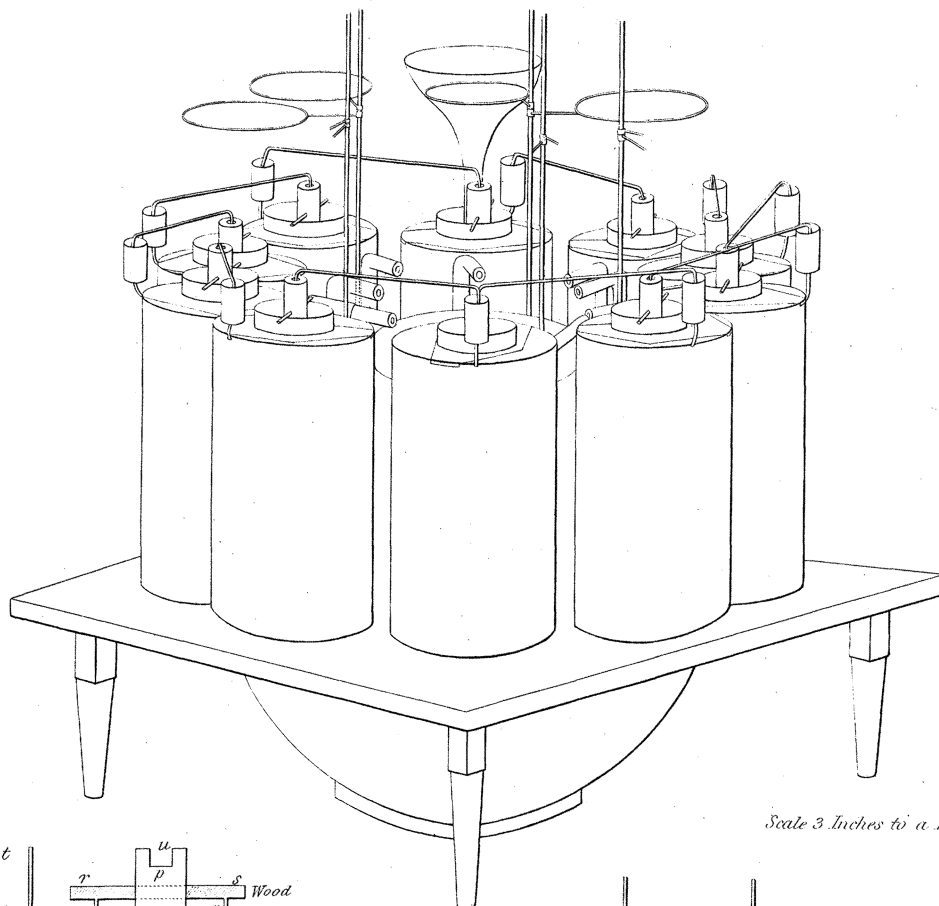
itself downwards and laterally at the same rate, till in a few hours it reached the edge of the plate. It then made its appearance upon the opposite surface, and ultimately both sides were completely coated; but the deposition decreased in thickness as it receded from the central zinc. This effect, in a voltaic combination, of a small generating surface upon a large conducting one, is strikingly contrasted with the result when we reverse the circumstances of the arrangement; for by causing a rod of platinum to rest by its end upon a large surface of amalgamated zinc, covered with the acidulated water, hydrogen of course escapes from the former metal; but the oxidation of the latter is so local, that a hole is eaten through it at the point of contact.

These experiments set the question at rest which they were meant to resolve; and I think, upon attentively considering the matter, that we may find the cause of this great diffusion of the hydrogen in that force of *heterogeneous adhesion* to which I have already referred the power of nascent gases, reacting upon, or acting in conjunction with, its elastic or self-repulsive force. Under the influence of these two forces the gaseous matter seems to extend itself upon the metal, much in the same way that a drop of volatile oil spreads itself over a large surface of water; and it seems not improbable that the efficiency of the conducting plates of voltaic arrangements may in part, if not wholly, depend upon the extent of surface which they afford for this diffusion of the gas, by which it is carried beyond the sphere of reaction upon the generating plates. To test the accuracy of this hypothesis, I reduced the width of the zinc plates in the battery; and beginning by halving, and then diminishing them to a quarter of their original dimensions, I ultimately found that amalgamated wires of one eighth of an inch diameter and three inches long, were as efficacious as the inch-wide plates; and that under their influence the conducting plates evolved as much gas in equal portions of time as when connected with the larger generating surfaces.

Amongst the numerous experiments which I have tried by the substitution of different metals, both as generating and conducting plates, for the normal plates of the battery, I must only detain you on the present occasion with the results of two. The first was the change of common zinc plates for the amalgamated, when strong local action took place, which, however, did not appear to interfere with the current affinity when the cells were connected in single series; for while the disengagement of hydrogen from the zinc was at the highest, as much gas was evolved from the platinum as when they were combined with the amalgamated metal.

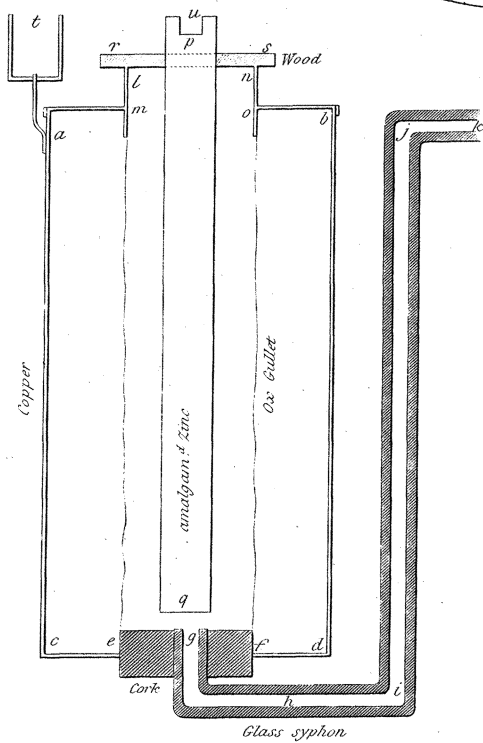
The second was the substitution of wrought iron for the amalgamated zinc plates. I had expected, from theoretical speculations upon its low equivalent number, that iron would have proved a very efficient generating metal; and my surprise was great upon discovering that its action in the battery was almost null. A slight local action took place upon the plates themselves, but the evolution of gas from the platinum was scarcely apparent, and quite immeasurable. This being the case, I converted them into conducting plates by removing the platinum, and opposing to them amalgamated zinc plates; and I was no less surprised to find that in their new office they

Fig. 2.



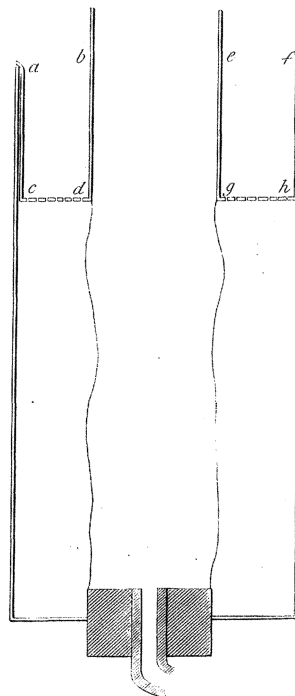
Scale 3 Inches to a Foot.

Fig. 1.



Scale 6 Inches to a Foot.

Fig. 3.



Constant Battery.

greatly exceeded in efficiency the platinum plates themselves; the quantity of gas collected in the voltameters in series being nearly double in amount to that from the battery in its normal state.

I repeated this experiment with fresh iron plates, and ascertained that previous opposition to the platinum had greatly contributed to this energetic action of the first set: the disengagement of gas from the second but little exceeded that from the normal plates.

I am inclined to believe that we may again find the explanation of these phenomena in the attraction of heterogeneous adhesion; and I think it probable that the hydrogen gas adhering with less force to the surface of the iron than to that of platinum, is more readily carried out of the sphere of action when evolved in the process of circulation upon the former than upon the latter. The efficacy derived from the previous combination of the iron with platinum may be ascribed to the cleansing of its surface, or possibly to some difference of mechanical structure developed in this particular position.

My attention was next turned to the effects of certain changes in the condition of the electrolyte employed in the excitation of the battery; and now it was that I began to experience those, apparently capricious, changes in the force of the current which soon obliged me to give up all hope of rendering the results comparable with one another in the present form of its construction. When I added to the acidulated water a volume of nitric acid equal to that of the sulphuric acid employed, the quantity of hydrogen evolved from the conducting plates of the cells was greatly diminished, and was irregular; but when the voltameter was substituted for one of the cells, the quantity of hydrogen which it indicated was at first nearly treble that from the battery in its normal state. This action, however, speedily declined by a quantity which was quite appreciable at intervals of five minutes. By breaking the connexion of the circuit this energy was partially recovered, and that even during the short cessation of action which arose from the mere turning of the voltameter. When the charge of nitric acid was increased, the evolution of hydrogen from some of the cells was wholly stopped, whilst in others it continued to a small but unequal amount; the quantity of the circulating current was at the same time increased, but rapidly declined as the action continued.

My efforts were now turned to discover the cause of this perplexing variation; but I shall not trouble you with the numberless experiments which I made upon the subject, any further than may be necessary to elucidate the steps by which I was ultimately led to its detection. I allowed the battery to exhaust itself by leaving it in connexion for thirty hours, at the expiration of which time scarcely any gas was evolved in the voltameter. I then removed the platinum plates and substituted fresh plates of the same metal; and when the connexions were made, the action was renewed with nearly the same activity as at the first; the falling off, however, was

rather more rapid than before. Even iron plates when substituted for the exhausted platinum renewed the action with great effect.

The decline thus seemed to depend upon some state taken up by the conducting plates, and this I endeavoured to remove in various ways. I polished them with rotten stone; I heated them red hot; and I boiled them in a strong solution of potassa, but without any decided effect. Boiling them, however, in nitric or muriatic acids completely restored them. Thus, frequently renewing the plates but retaining the old charge of acidulated water, the first action was always very brisk, but lasted for shorter and shorter periods, till the decline at last became almost immediate. Upon examining the plates after a long-protracted action of this kind, I found a roughness upon their edges and faces which conveyed the idea of a corrosion of the platinum. A more attentive investigation proved this to arise from a deposition upon them of metallic zinc; and upon leaving the battery in connexion for eighteen hours the coating increased to such a degree that it could be detached in large flakes. The precipitated metal was deposited chiefly upon the surface opposed to the zinc plate, but in some had extended considerably on the opposite side. It had mostly a beautiful mammillated appearance; but in one or two instances a crystalline structure was visible with a lens. I ascertained the weight of zinc thus deposited upon a plate by removing it with an acid, and found it 27·86 grains. The metal was pure, and when detached did not dissolve in the dilute acid till touched with a piece of platinum, when abundance of hydrogen gas was immediately given off from the latter. A similar deposition, in equal abundance, was formed upon iron when the conducting-plates were made of that metal. It originated doubtless from the oxide of zinc formed by the action of the battery at the generating-plate, and reduced by the *nascent* hydrogen on the conducting-plate; and its varying quantity and accumulation was amply sufficient to account for the variations and ultimate annihilation of the circulating force. In some instances, indeed, the casing of the platinum was so entire as to have the complete effect of one zinc surface opposed to another. This local deoxidating power of the hydrogen is exerted upon every oxide within its reach, and is more or less injurious to the action of the battery according as the resulting deposition upon the plates is more or less capable of generating a counter current by its reoxidation. The most injurious of all precipitations must, of course, be that of zinc upon the conducting-plate; and it must take place with a rapidity proportioned to the quantity of oxide held in solution by the electrolyte. In the common construction of the voltaic battery the solution of the metal is very rapid, on account of the local as well as the current action, and the deoxidating action must very soon be established; and the reason of the incrustation of zinc never having been remarked, is doubtless the extreme facility with which it is redissolved upon breaking the circuit. By its close contact with the copper it forms simple voltaic circles, and is under circumstances the most favourable for its removal. The momentary recovery of the strength of the

battery by breaking the metallic contact is now perfectly intelligible ; and we can no longer be at a loss to understand all the phenomena of RITTER's secondary piles, the effects ascribed to polarity by M. BECQUEREL, and the experiments of MARIANINI and A. DE LA RIVE upon this interesting subject.

I have remarked in the dissected battery, that when any oxide of copper was present in the solution, it was thrown down in preference to the oxide of zinc ; and that plates which had become covered with the former metal were, in some degree, protected from depositions of the latter. Upon adding, however, sulphate of copper in any considerable quantity to the liquid in the cells, notwithstanding the amalgamation of the zinc, there was local action enough upon that metal to disengage hydrogen ; which, in however small a quantity, was sufficient to commence the precipitation of the copper upon it. Single circles were thus immediately formed by the two metals, and local action increased to such a degree as speedily to cover the zinc with reduced copper. The addition of nitrate of mercury is not liable to the same objection ; and when I made use of this salt in the cells, the platinum plates soon became covered with metallic mercury in such quantities as ultimately to fall from them in drops. I did not carry this experiment far enough to ascertain whether the oxide of zinc would ultimately have become reduced with the oxide of mercury : but on one occasion, when some oxide of copper was present, the platinum plate became incrustated with a beautiful white soft amalgam ; which upon analysis proved to be an amalgam of copper.

Notwithstanding the unfavourable effect upon the circulating force of this secondary deoxidating power of the *nascent* hydrogen, where the ultimate result is the deposition of a solid body having a strong affinity for the oxygen of the electrolyte, there can be no doubt that the removal of the hydrogen by combinations which do not give rise to such precipitation greatly promotes the efficiency of the current : and I have had abundant opportunities of confirming your explanation of the good effects of the addition of nitric acid to the battery-charge by its abstraction of the hydrogen*. It is, moreover, quite certain, that not only does the oxygen of the acid act in this way as a *dehydrogenating* agent, but the nitrogen also ; for by neutralizing the exhausted charge of one of the cells of the battery with carbonate of soda, I not only obtained abundance of ammonia by distillation with lime, but a copious precipitate of ammonio-muriate of platinum with a solution of the chloride of that metal.

Having thus detailed, I hope sufficiently, the progressive steps by which I was led to the discovery of the cause of the variations and decline of the force of the voltaic battery, as well as of certain principles upon the application of which I have relied for the counteraction of its injurious effects, I will not detain you with any account of the less successful attempts which I made for that purpose, but proceed at once to describe a voltaic combination which I trust you will think worthy of the name of the CONSTANT BATTERY.

Fig. 1. of Plate IX. represents a section of one of the cells, ten of which are shown

* Experimental Researches (1021.).

in connexion at fig. 2.: (*a b c d*) is a cylinder of copper six inches high and three and a half inches wide; it is open at the top (*a b*) but closed at the bottom, except a collar (*e f*) one and a half inch wide, intended for the reception of a cork into which a glass siphon-tube (*g h i j k*) is fitted. On the top (*a b*) a copper collar corresponding with the one at the bottom rests by two horizontal arms. Previously to the fixing of the cork siphon-tube in its place, a membranous tube formed of a part of the gullet of an ox is drawn through the lower collar (*e f*) and fastened with twine to the upper (*l m n o*); and when tightly fixed by the cork below, forming an internal cavity to the cell communicating with the siphon-tube in such a way as that when filled with any liquid to the level (*m o*) any addition causes it to flow out at the aperture (*k*). In this state, for any number of drops allowed to fall into the top of the cavity, an equal number are discharged from the bottom. (*p q*) is a rod of cast zinc amalgamated with mercury, six inches long and half an inch diameter, supported on the rim of the upper collar by a stick of wood (*r s*) passing through a hole drilled in its upper extremity: (*t*) is a small cup for the reception of mercury, by which, and the cavity (*a*) at the top of the zinc rod, various connexions of the copper and zinc of the different cells may be made by means of wires proceeding from one to the other.

In fig. 2. the ten cells are represented as connected in single series, the zinc of one with the copper of the next. They stand upon a small table in a circle with the apertures of the siphon-tubes turned inwards, surrounding a large funnel communicating with the basin underneath for the reception of any liquid which may overflow. A smaller funnel is supported over the internal cavity of each cell by a ring sliding upon rods of brass placed between each pair of cells. One of these only is shown in the drawing to avoid the crowding of the sketch.

In the construction of this battery, I have availed myself of the power of reducing the surface of the generating plates to a *minimum*, the effective surface of one of the amalgamated zinc rods being less than ten square inches, whilst the internal surface of the copper cylinder to which it is opposed is nearly 72 square inches. My principal objects have been, to remove out of the circuit the oxide of zinc, which has been proved to be so injurious to the action of the common battery, as fast as its solution is formed, and to absorb the hydrogen evolved upon the copper without the precipitation of any substance which might deteriorate the latter.

The first is completely effected by the suspension of the rod in the interior membranous cell, into which fresh acidulated water is allowed slowly to drop from the funnel suspended over it, and the aperture of which is adjusted for the purpose; whilst the heavier solution of the oxide is withdrawn from the bottom at an equal rate by the siphon-tube. When both the exterior and interior cavities of the cell were charged with the same diluted acid, and connexion made between the zinc and the copper by means of a fine platinum wire $\frac{1}{1000}$ th of an inch in diameter, I found that the wire became red hot, and that the wet membrane presented no obstruction to the passage of the current.

The second object is attained by charging the exterior space surrounding the membrane with a saturated solution of sulphate of copper instead of diluted acid: upon completing the circuit the current passed freely through this solution; no hydrogen made its appearance upon the conducting plate, but a beautiful pink coating of pure copper was precipitated upon it, and thus perpetually renewed its surface.

When the whole battery was properly arranged and charged in this manner, no evolution of gas took place from the generating or conducting plates, either before or after the connexions were complete; but when a voltameter was included in the circuit, its action was found to be very energetic. It was also much more steady and permanent than that of the ordinary battery; but still there was a gradual, but very slow, decline, which I traced at length to the weakening of the saline solution by the precipitation of the copper, and the consequent decline of its conducting power.

To obviate this defect, I suspended some solid sulphate of copper in small muslin bags which just dipped below the surface of the solution in the cylinders; which gradually dissolving as the precipitation proceeded, kept it in a state of saturation. This expedient fully answered the purpose, and I found the current perfectly steady for six hours together. This arrangement I have since improved by placing the salt in a perforated colander of copper fixed to the upper collar.

Fig. 3. represents a section of this additional arrangement. (*a c f h*) is the colander with its central collar (*b d e g*), which rests by a small ledge upon the rim of the cylinder. The membrane is drawn through the collar, and turning over its edge is then fastened with twine.

After this alteration, the effective length of the zinc rods exposed to the action of the acid was found to be no more than four inches and a quarter. In ascertaining the powers of the battery in single series, the voltameter was the same that I have already described; the specific gravity of the solution of sulphate of copper was found to be 1198.5, and I commenced my experiments with the standard sulphuric acid, specific gravity 1027.3.

With this charge, after the circuit had been completed for ten minutes, the mean quantity of mixed gases taken at intervals of five minutes for two hours was 2.1 cubic inches, the results never varying more than 0.1 cubic inch from one another. The battery was then left in connexion, without the voltameter, for two hours, and again examined for three intervals of five minutes, when the mean quantity of gases was found as before. It was again left in connexion for two hours, and re-examined with the same result.

Upon adding nitric acid to the solution of sulphate of copper, I found that an injurious effect was produced; and that the mean quantity of gas in five minutes was lowered to 1.1 cubic inch: at this rate of action the battery, however, remained steady for six hours.

Returning to the original solution of sulphate of copper for the exterior cavity of the cells, I doubled the strength of the dilute acid for the interior; adding, for this

purpose, $4\frac{1}{2}$ measures of oil of vitriol to 100 measures of water, sp. gr. 1056·2, and found the mean quantity of gas evolved in the voltameter increased to 3·8 cubic inches per five minutes. I then removed the meter, and connected the circuit, leaving the battery in action for four hours. Upon replacing the meter it was ascertained to be still working at the same rate. The addition of nitric acid to the solution of the sulphate again reduced the rate to 2·1 cubic inches.

I now made trial of an addition of nitric acid to the interior liquid of the cell, adding an equal volume to that of the sulphuric acid, and restoring the solution of the neutral sulphate to the exterior division. At the first impression, an increased effect seemed to be produced, and the action for the first quarter of an hour was as high as 4·2 cubic inches per five minutes; but it ultimately settled down, and remained at the former amount without the nitric acid, of 3·8 cubic inches.

Here I may remark, that at the first immersion of the rods the effect of the battery is always a little higher than it afterwards settles at: and this I found to depend upon the evolution of a small quantity of hydrogen from a residue of local action upon the zinc, which adhered to its surface, and slightly impeded the action of the acid. These bubbles scarcely ever rose to the surface, and after the first quarter of an hour the battery took up a steady rate of action. By gently agitating the rods in the acid, the action would momentarily return to its original amount, but always settled down to the lower rate.

How very small this local action is will be seen from the details of the following series of experiments, which I shall give at length. Upon this occasion I weighed the ten zinc rods, which were the same which I had used from the first, and were reduced to nearly half their original circumference, that I might judge how nearly the zinc oxidated would be equivalent to the volume of gases evolved: their weight was $2\frac{1}{4}$ lbs. and 13 grains (15,763 grains). I trebled the strength of the acid, adding $6\frac{3}{4}$ measures of oil of vitriol to 100 measures of water, sp. gr. 1079·4. I sometimes made use of a large voltameter, the plates of which were 3 inches by 1 inch, and which, having a bent tube, admitted of my receiving the gases into a large graduated jar, and sometimes of the same small meter which I had hitherto employed. The results are contained in the following Table.

Large Voltameter.			
Time.	Quantity of Gas.	Rate per quarter of an Hour.	Rate per five Mi- nutes.
h m	cubic inches.	cubic inches.	cubic inches.
11 24			
11 39	16	16	5.3
11 45			
11 60	30	14	4.6
12 3			
12 18	44	14	4.6
12 19			
12 34	58	14	4.6
12 49	71	13	4.3
Small Voltameter.			
12 51			
12 56	4.6
12 58			
1 3	4.6
Hydrogen removed by agitating the Rods.			
1 6			
1 11	4.9
Large Voltameter.			
1 14			
1 29	85	14	4.6
1 31			
2 1	27	13.5	4.5
2 31	54	13.5	4.5
3 1	82	14	4.6
Small Voltameter.			
3 2			
3 7	4.8

Thus the total quantity of mixed gases collected amounted to 186 cubic inches, which, being corrected for pressure, were equal to 188.48. The zinc rods were removed from the cells, rinsed in water, and carefully dried, when they were found to have lost 933 grains.

Now adopting the data for computation, as laid down in your Tenth Series (1126.), of 100 cubic inches of the mixed gases being equivalent to 12.68 grains of water, and taking the equivalent number of water as 9, and that of zinc as 32.5, we have the following proportions :

$$\begin{array}{ccccccc}
 \text{Mixed Gases.} & & \text{Water.} & & & & \\
 \text{cub. inch.} & & \text{grs.} & & \text{cub. inch.} & & \text{grs.} \\
 100 & : & 12.68 & :: & 188 & : & 23.84,
 \end{array}$$

and

$$\begin{array}{ccccccc}
 \text{Equiv. Water.} & & \text{Equiv. Zinc.} & & & & \\
 & & & & \text{grs.} & & \text{grs.} \\
 9 & : & 32.5 & :: & 23.84 & : & 86.1;
 \end{array}$$

showing the quantity of zinc equivalent to 188 cubic inches of the mixed gases to be 86.1 grains; differing from the quantity actually consumed in each cell only 7.2 grains, or 2.3 for each equivalent. The waste of metal, indeed, must have been even smaller than this; for at the bottom of the cells I found a small quantity of amalgam, which had fallen off the rods, and which, at the time, it was not convenient to collect, but which, if added to the weight, would have materially diminished the deficiency.

For this quantity of zinc, 166.5 grains of metallic copper must have been precipitated on each copper cylinder; for not a bubble of hydrogen made its appearance upon them, and 6623 grains of crystallized sulphate of copper must have been consumed in the whole battery, or only 377 grains short of a pound avoirdupois.

Upon examining the cells after the course of experiments, the fresh-precipitated copper had a most beautiful appearance, being of a bright pink colour. It was not only deposited upon the sides and bottom of the cylinders, but upon the under surface also of the colanders. In the angle formed by the junction of the bottoms with the sides and at the contact of the membrane with the collars of the cullenders, it was collected in the largest quantities, and had a very distinct mammillated structure. At these points it is probable that the diffusion of the hydrogen had been impeded, and it had consequently accumulated in greatest abundance.

The charge of sulphate of copper has been left for weeks together in the battery, only taking care to keep the bottom of the colanders covered with the solid salt; but the acidulated water was withdrawn from the interior tubes every morning by means of a siphon, and a fresh charge substituted. It was generally found very slightly tinged with the sulphate, which would have been injurious to the zinc rods.

The only disadvantage that I am aware of in this new construction of the battery, is the unavoidable distance of the generating from the conducting metal, which is five or six times greater than in the double WOLLASTON plates; and this I sought to obviate as much as possible by improving the conducting power of the interposed electrolyte. I made trial of sulphuric acid of four times the standard strength, or 9 volumes of oil of vitriol to 100 of water, sp. gr. 1.1054; and this I worked for six hours continuously, and found the result very steady; 5.0 cubic inches with the large voltameter, and 5.5 by the smaller, per five minutes of time.

Taking into consideration the great precipitation of the sulphate of copper, I am doubtful whether the solution could be kept in a state of saturation at much beyond this rate of work; and in cases where it may be desirable to maintain a constant action for a great length of time, it may not be desirable to carry it even so far; but this, with many other questions, I must leave for future examination.

Being now desirous to bring the *constant battery* into more immediate comparison with one of the usual construction, I took a trough with ten WOLLASTON plates four inches square, which had been but little used, and carefully cleaned and fitted a double case of copper to the last zinc, to make the series complete. I charged it with a mixture in the proportions of 100 water, $2\frac{1}{4}$ oil of vitriol, and 2 nitric acid, and

set it to work with the small voltmeter. The following Table contains the results measured at intervals of five minutes.

Time.	Quantity of Gas.	Rate per 5 min.	Time.	Quantity of Gas.	Rate per 5 min.
h m	cubic inches.	cubic inches.	h m	cubic inches.	cubic inches.
10 22			11 24	1.3	1.3
10 27	2.5	2.5	11 29	2.2	0.9
10 32	4.6	2.1	11 34	3.0	0.8
10 34	Voltameter refilled.		11 39	3.55	0.55
10 39	2.6	2.6	11 44	4.1	0.55
10 44	4.4	1.8	11 49	4.5	0.4
10 46	Voltameter refilled.		11 54	4.9	0.4
10 51	2.8	2.8	11 59	5.25	0.35
10 56	4.9	2.1	12 0	Voltameter refilled.	
10 57	Voltameter refilled.		12 15	0.9	0.3
11 2	2.4	2.4	12 30	1.7	0.26
11 7	4.2	1.8	12 45	2.25	0.26
11 8	Voltameter refilled.		1 0	2.75	0.25
11 13	1.8	1.8	1 58	Battery left in connexion.	
11 18	3.2	1.4	2 13	0.1	0.03
11 19	Voltameter refilled.				

This series of observations displays in a striking manner the peculiar irregularities of the common voltaic battery, and entirely agrees with those which I had previously made with the dissected battery; the energy of the first contact declining even in the first five minutes a fourth or a third; recovering itself again by one minute's rest, and again declining: even with five such intervals of interrupted action, falling off permanently one half in the first hour; in the next hour of unceasing action rapidly falling to one tenth; and after four hours' connexion almost entirely ceasing.

If we compare the surfaces of the generating and conducting plates in each cell of the two batteries, we shall find that of the zinc in the WOLLASTON battery 32 square inches, whilst in the constant battery it does not exceed $7\frac{1}{2}$ inches. If we calculate only the interior surface of the copper of the former, that is also 32 inches; but if both surfaces be efficient, (as I believe, though not to the same amount,) then it amounts to 64 inches. It can only, of course, be the interior surface of the copper cylinders of the *constant battery* which assists the action; and reckoning $5\frac{1}{2}$ inches in depth to be efficient, it amounts to $65\frac{1}{2}$ inches; to which if we add a small quantity for the bottom and the underside of the colander, the amount of surface but little exceeds the former; but then it is all disposed to the greatest advantage. Under these circumstances the power of the constant battery is double that of the common battery at its first impulse, and can be maintained for any length of time in an inviolable condition.

I shall trouble you, on the present occasion, with but one comparison more; and that is, of the efficiency of the two batteries under a retarding force. The charge which I used for the *constant battery* was only the double acid (sp. gr. 1.056); but nevertheless I found that, with the opposition of three voltmeters, the amount of gases in each was 0.9 cubic inch per five minutes; whilst a fresh set of WOLLASTON plates, with a new charge in the same proportions as before, gave only 0.32 cubic

inch in the first five minutes: so that the superiority of the former, under these circumstances, was even greater than before.

I will only add, that I have kept six inches of platinum wire, $\frac{1}{1000}$ th of an inch diameter, permanently red hot for a considerable length of time when the battery was merely connected in single series, and that the spark between charcoal-points is remarkably beautiful; and shall reserve for a future communication, if you will permit it, some observations upon the different modes of combining the plates, for which it affords great facilities, and the different important applications to which, from the invariableness of its action, it is applicable.

My principal object in these researches has been the attainment of this constancy; but, in addition, this new combination will be found, I think, to possess advantages which will secure to it a more general application than I at first contemplated.

First, the abolition of all local action by the facility of applying amalgamated zinc:

Second, the trifling expense of replacing, the zinc rods when worn out (for they are easily cast and fitted in the laboratory); and the total absence of any wear of the copper:

Third, the non-necessity of employing nitric acid, and the substitution of the cheaper materials, sulphate of copper and oil of vitriol; to which I may add, the absence of any annoying fumes:

And, fourth, the facility and perfection with which all metallic communications may be made, and different combinations of the plates arranged.

Hoping that I may not have wearied you by these details,

I remain, dear FARADAY,

Your very faithful friend,

J. F. DANIELL.

*King's College,
23rd January, 1836.*