

XI. *Additional Observations 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,

THE Council of the Royal Society having done me the honour to order the publication of my observations upon “Voltaic Combinations” in the *Philosophical Transactions*, I should wish to add the results of some further researches, which may render the account of the *constant voltaic battery* more complete and practically useful.

My great object in this combination was to obtain an invariable current of force sufficient to effect chemical decompositions, after overcoming the resistance necessary to register its quantity by the voltameter; and having succeeded in this, it seemed to me almost a matter of indifference to the solution of the various important questions to which it might be applied, whether the quantity were large or small. I quickly, however, discovered that the battery might be rendered not only perfectly steady in action but very powerful; and that it would be extremely efficient and convenient for all the purposes to which the common voltaic battery is usually applied. I set myself therefore to perfect its construction with this view.

Before I state the results I wish to direct your attention to some observations which affect the construction and application of your voltameter, being convinced that anything which may tend to facilitate the use or establish the correctness of that most important instrument will prove of substantial benefit to electro-chemical science. In my previous communication (p. 112) I stated that I had found that the plates of a voltameter only six eighths of an inch wide evolved the same amount of gases as two platinum plates one inch wide, and of the same height, in one of the cells of the dissected battery, when the former was substituted in the circuit for the latter; and I imagined that “their nearer approximation had counterbalanced their deficiency of surface.” The results of the experiments recorded in the Table (p. 121), also show that there was no difference in the indications of the same small meter and those of a larger, the plates of which were three inches by one inch when they were alternately used. The plates of the larger instrument were moveable, and admitted of adjustment to different distances from each other; and by these means I ascer-

tained that no alteration, within the distance of the generating and conducting plates of the battery, produced any difference in the results.

This rendered the non-influence of variation of surface still more remarkable; and wishing to push the observation to the utmost, I reduced the plates of a voltmeter to the width of one eighth of an inch, retaining the same height of three inches, and still found its efficacy unimpaired. I next thrust two platinum wires one tenth of an inch diameter through a cork closing the mouth of a glass tube, exposing about two inches of each to the dilute acid without any diminution of effect, the battery generating in all these experiments at the rate of 2·7 cubic inches per five minutes.

When I even covered the wires with a resinous cement so as to have only one fourth of an inch of each exposed, the gases evolved in the same time amounted to 2·3 cubic inches. I ultimately coated the wires entirely with cement, and carefully bared their mere points with a file, when they still gave off the gases at the rate of 0·8 cubic inch per five minutes; and in this case the currents of the gases instead of rising at once from the points of the horizontal wires seemed to be projected forward into the liquid with some force. This independence of the results upon the metallic surfaces of the voltmeter is curiously contrasted with the paramount influence of the surface of the conducting plates of the cells of the battery, but is probably owing to the absence of any active chemical affinity assisting or retarding the main current which circulates.

In the prosecution of my experiments I now began to perceive that it was by no means necessary to attend so closely to the supply of fresh acid to the battery as at first seemed advisable; and I ascertained that after an uninterrupted action of five hours, without its renewal, the voltmeter only indicated a decline from 2·7 to 2·4. It being of great consequence to note to what extent the constancy of the action might be independent of the exact adjustment of the acid, I left the battery in connexion for twenty-four hours, at the expiration of which time 0·9 cubic inch of the mixed gases was collected in the voltmeter in a quarter of an hour, or 0·3 cubic inch per five minutes. The acid was found to be almost perfectly saturated; a very small drop of dilute ammonia occasioning an instantaneous precipitation of oxide of zinc in the solution, which had a specific gravity of 1·276. In this state three quarters of a fluid ounce of fresh dilute acid was poured upon the top of the solution in each cell (the total charge of each cell being about $5\frac{1}{2}$ fluid ounces), when the action not only rose to its original amount of 2·7 cubic inches, but to 4·2 cubic inches, at which rate of work it kept perfectly steady without any further renewal of the acid for four hours.

This increase of action I could only refer to the superior conducting power of the solution of sulphate of zinc; and two important points were thus indicated: 1st, that the conducting power of the electrolyte in the battery might be increased with great advantage; and 2ndly, that the quantity of the circulating force was still more independent of the surface of the generating metal than my experiments had yet shown

it to be. The length of the zinc rods exposed to the action of the fresh acid, which must have floated upon the saline solution in this experiment, could not much have exceeded one inch, and yet they proved perfectly efficient. I immediately confirmed this conclusion by shortening the zinc rods to one fourth of their original length, and found no diminution of the power of the battery when charged with fresh acid.

I next charged the battery with acid of the same strength as that which I employed in the voltameters, viz., eight parts of water to one part of oil of vitriol by measure (specific gravity 1136), and obtained at once a steady action of 11· cubic inches per five minutes; this was therefore the mixture which I employed in all my subsequent experiments.

This rate of action must obviously require some attention to the state of the solutions in the battery, when perfect steadiness is required to be maintained for a long period; as nearly 25 grains of oxide of zinc are formed, and 154 grains of sulphate of copper decomposed in each cell per hour. Nevertheless it will remain constant for an hour and a half even without any change of acid; and the addition every now and then of one fluid ounce of fresh acid will maintain the action for any desired time, provided the colanders be kept well supplied with the salt of copper.

Considering the great advantage which had been derived from the extension of the surface of the conducting metal of the battery, I now wished to ascertain whether this might be carried further; and for this purpose I caused some cells to be fitted up in the interior with ten small plates, one inch wide, extending from the bottom to the colander, and converging from the interior circumference towards the centre. In this way they just reached to the membranous tube, and the surface of the copper was more than trebled. I thought it possible that advantage might be thus derived, not only from the great extension of surface, but from the approximation of a part of the conducting plate to the generating rod.

My first experiment was made with five plain cells and five ribbed, working into separate voltameters, and I found the products equal, inclining, if anything, in favour of the former. The amount of gases from each was, however, only 5·5 cubic inches per five minutes, or one half of that from the whole series of ten cells. When the ribbed and the plain cells were connected together in one series, the amount in one meter was, as before, 11 cubic inches.

It now seemed evident that a series of five did not confer *intensity* enough upon the current to enable its whole quantity to overcome the resistance of the conducting fluid between the two metals at the existing distance; and this being the case with the plain cells, no increase of quantity could be expected to manifest itself from those with extended surfaces. When the latter were joined with the former, the smaller surface of course governed the whole series according to the established law. I therefore completed the number of the ribbed cells to ten, and setting them to work against an equal number of plain, the product of the latter was, as before, 11· cubic inches, but that of the former did not exceed 8·5. I have not yet been able to satisfy

myself, whether this unexpected difference, in the opposite direction to what I expected, is dependent upon the construction of the cells or upon some accidental circumstance which I have not been able to trace; but the result may certainly be taken to prove that no advantage arises from the extension or approximation of the conducting metal which I have described.

The increase of the number of the battery series requires for convenience a different arrangement from that which I described in my last communication; and I now place the cells in two parallel lines of ten each, upon a long table, the siphon-tubes arranged opposite to each other, and hanging over a small gutter placed between the rows, to carry off the refuse solution when it is necessary to change the acid; and as the uniformity of action may be completely maintained by the occasional addition of a small quantity of fresh liquid, I have been able to dispense with the cumbrous addition of the dripping funnels. This arrangement admits with facility of any combination of the plates which may be desired.

I proceeded now to connect the cells together in pairs; the zinc rod of each ribbed cell being in communication with that of a plain cell, and the copper with the copper. The ten pairs were then connected in a series of ten: the product of this combination was 17 cubic inches per five minutes, or exactly double that of the single-ribbed cells.

Considered in a theoretical point of view, these experiments seem to me to lead to the conclusion that the most perfect voltaic combination would consist of a solid sphere of a generating metal, surrounded by a hollow sphere of a conducting metal, with a stratum of intervening electrolyte perpetually renewed, and the metals communicating by a wire defended from the electrolyte by a glass tube covering that portion which it would be necessary should pass through it. In such a hypothetical arrangement, the resistance of the electrolyte would increase directly as the distances of the two spheres, or as the thickness of the stratum; while, supposing this resistance overcome, the quantity of force set in circulation would increase as the square of that distance from the centre, or as the surface of the exterior sphere. The number of a series required to give the necessary impulse would consequently only increase as the simple distance, while the advantage would increase as the square.

The rod of zinc within the cylinder of copper is probably the nearest practical approximation which can be made to such an arrangement; but the soundness of this deduction might doubtless be tested by varying the diameters of the cylinders.

The battery which I have now described, consisting of twenty cells, will, I think, be found amply sufficient for all the purposes of demonstration and investigation. It is competent to keep eight inches of platinum wire $\frac{1}{1000}$ th inch permanently red hot in the open air; and the amount of work which it is able to perform renders it even an economical source of the purest oxygen for laboratory purposes.

To facilitate this application, I have fitted up a cell by inclosing a platinum plate, instead of the zinc rod, within the membranous tube, which is closed at the upper end by a glass tube bent in a convenient form to deliver the disengaged gas under a

receiver. When this cell is included in the circuit of double cells, the hydrogen is absorbed as before by the oxide of copper; but the oxygen is evolved at the rate of 84 cubic inches per hour.

I shall conclude these observations with the result of an experiment which places the secondary action of the affinities of the disengaged gases in a striking point of view. The mixed gases collected in a voltameter in five minutes were found to amount to 17 cubic inches; the oxygen collected in an equal time, when the hydrogen was absorbed, was 7 cubic inches; which are equivalent to 21 cubic inches of the mixed gases: and the hydrogen collected when the oxygen was absorbed (as is readily effected by reversing the connexions of the cell which I have just described) amounted to 16 cubic inches, equivalent to about 24 cubic inches of the mixed gases. Thus the removal of the hydrogen from the sphere of attraction allowed of an increase of action equal to 4 cubic inches, while the increase from the like removal of the oxygen was very nearly double; a difference which is probably referable to the equivalent combining volumes of the two gases. This observation opens a new field of inquiry of great interest, upon which, with your permission, I hope to have the pleasure of addressing you at no very distant period.

I remain, my dear FARADAY,

Yours very faithfully,

J. F. DANIELL.

*King's College,
6th April, 1836.*