

VI. *Fifth Letter on Voltaic Combinations, with some Account of the Effects of a large Constant Battery. Addressed to MICHAEL FARADAY, Esq. D.C.L. F.R.S., Fullerian Prof. Chem. Royal Institution, &c. &c. &c. By J. FREDERIC DANIELL, Esq. F.R.S., Prof. Chem. in King's College, London.*

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MY DEAR FARADAY,

IN my last letter to you, which the Royal Society have done me the honour to publish in the Philosophical Transactions for 1838, I observed, that “the principal circumstance which might be supposed to limit the power of an active point within a conducting sphere, in any given electrolyte, is the resistance of that electrolyte, which increases in a certain ratio to its depth or thickness.” The superficial measure of the conducting sphere, and the distance of the generating metal, or the depth and resistance of the electrolyte, are, in fact, the variable conditions in a voltaic combination upon which its efficiency depends; and their relations require further investigation before we shall be able to determine what may be the proper proportions for the economical application of the power to useful purposes. I shall venture, therefore, to trouble you with the results of some further experiments upon the subject, and upon different combinations of the constant battery, before I proceed to communicate some observations upon Electrolysis, which I trust you will find not without interest, and to which, according to my plan, my attention has been lately exclusively directed.

Looking, for a moment, upon the affinity which circulates in the battery as a radiant force, it seemed desirable to ascertain what would be the result of intercepting the rays by the conducting surface nearer to their centre than in the arrangements which have been previously described, as the relation of the generating and conducting metals to each other might be thereby more clearly ascertained.

For this purpose I constructed a battery of ten cylinders of copper, nineteen inches in length by $1\frac{1}{2}$ inch in diameter. As the quantity of acid and sulphate of copper which these cylinders could contain was but small, it was necessary to provide for the perpetual renovation of the charge as the zinc became dissolved and the copper precipitated. This was effected by connecting all the membranes which held the acid and the zinc rods, at their lower ends, with a pipe terminating in a stop-cock. Their upper ends were fixed in a cistern, from which they could be gradually supplied with fresh acid as the saturated acid flowed out below. All the exterior cells formed between the membranes and the copper cylinders also terminated below in a common reservoir, surrounding the former pipe, by which their exhausted contents could be

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drawn off, as a fresh supply of sulphate of copper was furnished from above by an exterior cistern holding the solution. When the battery was in action, a saturated solution of sulphate of copper, thus supplied from the top, could be drawn off almost colourless at the bottom; and it remained constant for a considerable time.

The effect produced was $4\frac{1}{2}$ cubic inches of mixed gases per minute, measured in the voltameter formerly described.

I compared this result with that obtained from a battery of ten cylinders, twenty inches in length and $3\frac{1}{2}$ inches in diameter, which gave in the same voltameter eleven cubic inches per minute. The surfaces of the conducting cylinders were respectively 89.5 square inches and 220 square inches; and the products of gas in equal times were nearly in the same proportion as the surfaces. The zinc rods were $\frac{1}{2}$ inch in diameter in both cases.

I next proceeded to compare two small hemispheres of copper with the large hemisphere of brass of $9\frac{1}{4}$ inches diameter, formerly described*. They were fitted up, as before, as single circuits, with a zinc ball of one inch diameter, first placed in a membrane below the surface of the solution of copper. The measure made use of was the calorific galvanometer; the first was four inches diameter, and produced a permanent effect of 45° upon the thermometer. The second, of $2\frac{1}{2}$ inches diameter, produced an effect of 29° . The effect of the large hemisphere was 90° . Here it will be observed that the action was by no means proportioned to the surfaces of the conducting hemispheres, but approximated more nearly to the simple ratios of their diameters.

Hence it would appear that the circulating force of both a simple and compound voltaic circuit increased with the surface of the conducting plate surrounding an active centre; but the experiments are not sufficient to determine the law of the increase.

I now constructed a battery of ten larger cylinders, of four inches diameter, the arrangement in everything being the same as before, and found that the action was reduced to one half, the amount of mixed gases in the voltameter per minute being only $5\frac{1}{2}$ cubic inches. The experiments were repeated several times, and the action maintained for several hours, and always with consistent results. This extraordinary and sudden decline of force requires further investigation; and indeed the only conclusion which we can at present draw from the experiments which I have just detailed, but which is of considerable practical importance, is, that cylinders of $3\frac{1}{2}$ inches diameter form much more effective conducting plates in a voltaic arrangement than cylinders of either greater or less diameter. It must, however, be borne in mind that this has only been proved with a series of ten cells; for it is highly probable that the limits of efficiency may change with the number of the series.

The following experiments with the different combinations which may be made with twenty cylinders, throw some light on the question of the influence of the numbers of a series, the diameter of the members of which is limited to $3\frac{1}{2}$ inches. The

* Philosophical Transactions, for 1838, p. 41.

cylinders were twenty inches in height, and the zinc rods were $\frac{5}{8}$ ths of an inch in diameter. The electrolyte consisted of eight parts of water and one part of oil of vitriol by measure, and in the exterior divisions of the cells was saturated with sulphate of copper. The temperature was about 65°; the duration of each experiment was one minute.

First Set of Experiments.

Number of cells	1	2	3	4	5	10	15	20
Cubic inches of gas	0	just visible	$1\frac{1}{8}$	$3\frac{7}{8}$	6	$12\frac{1}{4}$	$15\frac{1}{3}$	$17\frac{1}{4}$

Second Set of Experiments.

	All cells direct.	1 invert.	2 invert.	3 invert.	4 invert.	5 invert.
Cubic inches of gas	$17\frac{1}{2}$	$15\frac{1}{2}$	$12\frac{3}{4}$	$10\frac{1}{2}$	$8\frac{1}{2}$	$5\frac{1}{2}$
	6 invert.	7 invert.	8 invert.	9 invert.		
Cubic inches of gas	$3\frac{1}{2}$	$1\frac{5}{8}$	$1\frac{1}{8}$	just visible.		

Third Set of Experiments.

Number of double cells	5	10
Cubic inches of gas	11	20

Fourth Set of Experiments.

	5 triple cells.	5 quadruple cells.
Cubic inches of gas	$14\frac{1}{2}$	$15\frac{2}{3}$

When a series of five single cells was connected with a series of five double cells, and the same voltameter employed, the amount of gas was $14\frac{1}{2}$ cubic inches.

When two series of five double cells were each connected with the same voltameter, the amount of gas was $15\frac{2}{3}$ cubic inches. Each double series alone gave eleven cubic inches.

From these experiments it appears that the most advantageous adjustment of active force and resistance is in the series of ten single cells when they are of the diameter of $3\frac{1}{2}$ inches, and that the largest amount of work which can be derived from twenty such cells is when they are arranged in two series of ten; for

Cells.	Cubic in.	Cells.	Cubic in.	Cells.	Cubic in.
10 give	$12\frac{1}{2}$	5 give	6	4 give	$3\frac{7}{8}$
	2		4		5
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20 . . .	25	20 . . .	24	20 . . .	$19\frac{3}{8}$

Twenty in single series give $17\frac{1}{2}$ cubic inches. Ten double cells give 20 cubic inches.

Cells.	Cubic inches.	Cells.	Cubic inches.
5 double give	11	5 quadruple give	$15\frac{2}{3}$
	2		
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20	22	20	$15\frac{2}{3}$

I now combined in a single series a battery of seventy cells of the same dimensions, and charged in the same manner, for the purpose of observing chiefly the effects of light and heat produced by the current in a state of high intensity and constant action. The interior cells were formed of light porous earthenware, and answered their purpose perfectly, offering no more obstruction to the current than the membranes, and being much more convenient in use.

The quantity of decomposition per minute from a voltameter, with the usual charge of dilute acid, was only seventeen cubic inches; while with distilled water the passage of a current was scarcely indicated by a few bubbles of gas which rose from the electrodes.

The flame between charcoal points was of considerable volume, and formed a continuous arch when the points were separated to about three-fourths of an inch. This striking distance did not appear to be increased in a flask exhausted by the air-pump. The light and radiant heat were most intense, and proved highly injurious to the eyes of many of the party who did me the honour of assisting me in my experiments. In my own case, although protected by dark grey glasses of double thickness, a high state of inflammation was produced, which it required very active medical treatment to subdue; and, as you well know, in others, even the application of leeches was found to be necessary. The whole of my face was also scorched and inflamed as if it had been exposed for many hours to a bright midsummer sun. When reflected from an imperfect parabolic metallic mirror in a lantern, the rays were collected into a focus by a glass lens, and readily burned a hole in paper at many feet from their source. The heat was quite intolerable to the hand when held near the lantern.

Paper steeped in nitrate of silver, and afterwards dried, was speedily turned brown in the light; and when a piece of fine wire-gauze was held before it, the pattern of the latter appeared in white lines, corresponding to the parts which it protected.

The phenomenon of the transfer of the charcoal from one electrode to the other, which I believe was first remarked by Dr. HARE, was abundantly produced. The transfer took place from the zincode (or positive pole, or charcoal connected with the last copper cylinder of the battery) to the platinode (or negative pole, or charcoal connected with the last zinc rod of the battery*), and in the former a sharp, well-defined, cup-like cavity was produced, and on the latter, a corresponding protuberance or nipple. The carbon of the latter proved to be very hard, and had the rough mammillated structure of the carbon which is found coating the interior of gas retorts. When a platinum rod was substituted for the charcoal at the platinode, the transfer

* I have so strongly felt the want of some distinctive names for the two poles of the battery consistent with the principles of nomenclature which you have adopted, that I have ventured to propose those mentioned above, and have constantly used them in my lectures. The *anode* and *cathode* have relation to the surfaces of the electrolyte, and if we distinguish the electrodes themselves as the *anelectrode* and the *cathoelectrode*, confusion is apt to arise; I find practically that students easily recollect that the *zincode* is that electrode which in the regular battery would be constructed of zinc, and the *platinode* of platinum.

of the charcoal from the zincode still took place, and the metal became coated with carbon, which was beautifully moulded to its extremity. When this arrangement was reversed, and the zincode was formed of platinum, and the platinode of charcoal, particles of platinum were transferred, and the charcoal became covered with distinct and numerous globules of the fused metal.

The transfer of matter of such dissimilar kinds in this definite direction, renders it probable that it is essential to the disruptive discharge, and is entirely analogous to the transfer of matter which has been observed by FUSINERI in all cases of the Leyden discharge, and of the discharge of atmospheric electricity by lightning.

As connected with this subject I may recall to your recollection the attempts which we made to produce a spark before contact, and in which we reduced the distance between two platinum wires connecting the two ends of the battery, to the utmost possible degree, without success. Even when the wires were heated in the flame of a blow-pipe no discharge was established. At the suggestion of Sir JOHN HERSCHEL, I adjusted two brass balls connected with the two ends of the battery, within a very minute distance of each other, and, while in this situation, I passed the spark of a small Leyden jar between them, and immediately the battery current was established, and the brass balls, which were hollow, were burned. Is it not probable that the Leyden discharge in this case transferred the conducting matter which was essential to the existence of the voltaic flame, and which was afterwards supplied by its own energy?

The arch of flame between the electrodes was found to be attracted or repelled by the poles of a magnet according as one or other pole was held above or below it, as was first ascertained by Sir H. DAVY; and the repulsion was at times so great as to extinguish the flame. When, according to the suggestion of Mr. GASSIOT, the flame was drawn from the pole of the magnet itself included in the circuit, it rotated in a very beautiful manner*. When the zincode was connected with the marked pole, and the platinode was held over it, the rotation was from west to east, or in the contrary direction to the motion of the hands of a watch; but when the arrangement was reversed, and the zincode was connected with the unmarked pole, the rotation was reversed. The flame was also made to rotate by the induction of the magnetism of the earth upon a poker of iron held in the direction of the dip.

The experiment was again varied by leading the current through a spiral, twisted round a horse-shoe bar of soft iron, and causing the flame to rotate under the influence of its own magnetic force.

The heating power of the battery was very great, and the greater intensity of the heat on the side of the zincode than on that of the platinode extremely remarkable. Mr. GASSIOT first pointed out to me, that when two stout copper wires, of $\frac{1}{5}$ th of an inch in diameter, were connected with the extremities of the battery and held across each other, so that the flame passed between them, the wire at the zincode became

* This modification of Sir H. DAVY's experiment was first made, as I am informed, by Mr. STURGEON.

red hot, while the other remained comparatively cool. A bar of platinum, $\frac{1}{8}$ th of an inch square, freely melted and dropped in large globules in the former situation, but showed no signs of fusion at the platinode.

When the zincode was formed of the hard carbon taken from the gas retorts, and a cavity ground in it, the most infusible metals placed in it were melted in considerable quantities.

Pure rhodium immediately ran into a perfect globule, and burned with scintillations and a blue light. The native alloy of iridium and osmium, as well as pure iridium, were also completely melted. These metals were kindly supplied to me for the experiments by Mr. JOHNSTON.

Titanium fused instantly, and burned with scintillations very much resembling those from iron.

The native ore of platinum was completely fused; but the mass, when cold, proved to be very brittle.

After four hours constant action, the power of the battery was found to be undiminished, and the amount of the zinc consumed was very small.

In conclusion, I shall briefly describe the results of some experiments on the evolution of the mixed gases from water in a confined space, and under consequent high pressures, which I made from July to October 1837, and which I intended to have further extended. My objects were, to ascertain, 1st, in what manner conduction would be carried on, supposing that the tube in which the electrodes were introduced were quite filled with the electrolyte, and there were no space for the accumulation of the gases; 2ndly, whether decomposition having been effected, recombination would take place at any given pressure; and, 3rdly, whether any reaction on the current-force of the battery would arise from the additional mechanical force which it would have to overcome.

The first apparatus which I made use of was a stout glass tube, into the lower end of which a platinum wire was inserted to form an electrode. This end was hermetically closed, and the upper end ground and fitted with a platinum valve pressed upon by a lever, which could be loaded with weights to any required amount. From this valve a wire projected into the tube to form the other electrode. The tube was accurately filled with the standard dilute acid, and placed in the battery circuit with a voltameter, by which the rate of work and the quantity of the gases disengaged could be ascertained. The battery made use of consisted of ten large cells with the usual charge. Before pressure was applied, the rate of work was always ascertained with the tube and voltameter in their places. I tried many experiments with this arrangement; but it will only be necessary to describe the general results.

The pressure was carried up to 98 lbs. upon a circular area of $\frac{3}{4}$ inch diameter, the apparatus appeared to be quite tight for a long time, and bubbles of gas were evolved from the two wires when the circuit was complete. The liquid became hazy, and bubbles of gas seemed to line the tube. The stream of oxygen from the upper wire

was projected downwards into the liquid, as if with considerable force. The liquid ultimately oozed out between the edge of the tube and the valve, and the experiment was stopped. When the pressure on the valve was removed, a puff of gas took place and the liquid slowly effervesced for a considerable time, but was not projected with any violence. The compression tube felt warm to the hand but not very hot. The quantity of gas which first escaped seemed to bear but a small proportion to that which was indicated by the voltameter included in the circuit, and the rate of decomposition was not at all altered by the accumulation of the elastic force.

To carry the experiment as far as the resistance of glass could conveniently admit of, I caused a compression tube to be made of $\frac{1}{8}$ th inch in thickness, of the capacity of $1\frac{2}{10}$ th cubic inch. Two platinum plates were sealed into its lower end; one cubic inch of standard acid was poured into it, and it was then hermetically sealed at the top. It was placed securely in the battery circuit with a voltameter, and the progress of the experiment was watched from a safe distance.

The evolution of the gas, which was measured at short intervals, took place with perfect regularity, and did not appear to be in the slightest degree affected by the gradually increasing compression. In $4\frac{1}{2}$ minutes, when nineteen cubic inches had been collected, the compression tube burst with a loud explosion, and the fragments, which were very small, were scattered all over the laboratory.

If we were to calculate that nineteen cubic inches were compressed into the $\frac{2}{5}$ ths of a cubic inch space, unoccupied by the liquid, this would be a compression of sixty-three into one, and the pressure would amount to nearly 940 lbs. upon the square inch; but if we were to reckon, as was probably the case, that two cubic inches of the gases were kept down by the solvent power of the liquid at this high pressure, then the compression would have amounted to fifty-six into one, and the pressure to 840 lbs. upon the square inch.

It is probable that the means here pointed out might be applied with advantage to the compression of some of the gases whose liquefaction you have already effected; and I purpose, when my avocations will permit, to return to the experiments with this view.

I remain, my dear FARADAY,
Your faithful friend,
J. F. DANIELL.

*King's College, London,
April 9th, 1839.*