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

Received March 30,—Read April 6, 1837.

MY DEAR FARADAY,

I HAD intended, ere this, to have addressed you upon the subject of the *measure of affinity* which the *constant battery* may be made to supply, as indicated by the concluding experiment of my last letter; but my attention has been diverted, and the whole of my leisure occupied by what I found to be a necessary preliminary investigation of the effects of changes of temperature upon the voltaic action. In the course of my experiments upon this principal subject, I have also been led to observe some curious disturbances and diversions of the battery current, from secondary combinations; and I now submit the results of the whole inquiry to your judgment, not without a hope that you may consider them of sufficient interest and importance to be communicated to the Royal Society.

You may perhaps recollect that the standard charge, which I finally adopted in the use of the constant battery, was a mixture of eight parts of water with one of oil of vitriol on the side of the zinc, and a saturated solution of sulphate of copper in contact with the copper; and that the average amount of its work, as measured by the voltameter, was 11 cubic inches of mixed gases per five minutes. It occurred to me that the resistance to the current might again be reduced by dissolving the salt in the standard acid instead of water; and upon making the experiment I found the action increased from 11 cubic inches to 13 cubic inches, at which rate it steadily maintained itself; the following being the result of one series of observations.

Time.		Interval.	Voltameter.
h	m		Cubic inches.
11	0		
11	5	5	13
11	10	5	26
11	15	5	39
11	20	5	52

Upon one occasion I prepared the charge by adding one part of oil of vitriol to eight parts of the saturated solution of the sulphate, and poured it into the cells whilst of the high temperature produced by the disengagement of heat during the mixture, which was about 110°; and the following series of experiments will show the great increase of action which followed this accession of heat, and its rapid decline with the temperature. The observations were made at intervals of two minutes; but I have added the calculated rate per five minutes to facilitate comparison with former experiments.

Time.		Interval.	Voltameter.	5 min. rate.
h	m	′	Cubic inches.	Cubic inches.
12	52			
12	54	2	8·8	22·
12	59			
12	61	2	8·	20·
1	3			
1	5	2	7·3	18·2
1	7			
1	9	2	7·	17·5
1	11			
1	13	2	6·5	16·2
1	14			
1	16	2	6·	15·
1	17			
1	19	2	5·7	14·2
1	21	2	4·8	12·

Wishing to follow up this indication of the influence of temperature, I caused a tub to be made which would just receive the ten cells of the battery standing upon small blocks of wood, between which there was room for the syphon tubes to pass. In this situation it was fresh charged with the acid solution; and henceforth I carefully noted the temperature, which in this instance was 68°. Its action was steady for three quarters of an hour at 13·8 cubic inches per five minutes. Two fluid ounces of fresh standard acid were then poured into the inner cells, and the tub was filled with hot water of the temperature of 130° to nearly the top of the cells; the action was now found to be 20 cubic inches per five minutes. The temperature of the exterior solution of sulphate was 106°, and of the interior acid 100°. The experiment was terminated by the bursting of all the membranes which had been exposed for five weeks to the acid solution.

Having remounted the battery, I proceeded to ascertain the effect of different charges in connection with this decided influence of temperature; and, in the first place, having poured a plain aqueous solution of sulphate of copper into the exterior cells, I filled the interior with pure water, making use at the same time of fresh amalgamated zinc rods. At the commencement of the experiment the temperature was 74°; and there was no appreciable decomposition in the voltameter. The tub was then filled with water at 120°. When the temperature of the interior cell had reached 100° a slow action commenced, which became steady at 0·6 cubic inches per five minutes. The voltameter itself being now also heated to 115°, the following results were obtained:

Time. h m	Interval.	Voltameter. Cubic inches.	5 min. rate. Cubic inches.
11 21			
11 26	5	0·8	0·8
11 31	10	1·6	0·8
11 51	30	5·0	0·8

At the expiration of the experiment the rods were found to be only slightly tarnished, and no copper had penetrated to the interior cells.

The next charge which I made trial of was a solution of muriate of ammonia, in the proportion of two pounds of the salt to a gallon of water for the interior cells, and aqueous solution of sulphate of copper for the exterior. The results were as follow:

	per 5 min. Cubic inches.
At 74° out of water	5·5
At 94 in water	8·8
At 124 in water	12·5

Upon this occasion I first observed that a portion of the current was discharged by the water in which the battery was immersed.

The battery plunged in water of the atmospheric temperature of 74° had been working steadily for twenty minutes at the rate of 3·1 cubic inches per five minutes: when the water was drawn off from the tub the rate immediately rose, and was maintained at 4·2 cubic inches per five minutes.

That a discharge may take place from the copper of one cell to the copper of the next, when the regular circuit is interrupted between the two, I had many opportunities of observing in the powerful currents with which I had been experimenting; for I have frequently seen it pass in the form of a spark when the cells had been too much approximated in the air; and when in water it was indicated by the frothing between the two from the disengagement of gas. In such a case there is no doubt that one of the zinc rods is thrown out of action, and the copper of that cell merely acts as an electrode to the antecedent zinc. I shall hereafter point out to you how readily a portion of a current may be diverted from its principal course to by-paths, if I may so express myself, which may be open to it.

The decomposition of the secondary electrolytes, and the course of the ions in this combination, are worthy of some remark. In several instances when the battery had been in action for a considerable period, the zinc rods were found thickly studded with beautiful, large, transparent crystals of sulphate of zinc. The solution of this salt was abundantly precipitated by nitrate of baryta and by potassa, the precipitate in the latter case being redissolved by an excess of the alkali. It was not in the slightest degree affected by nitrate of silver; proving that no muriate or chloride existed in it. There were no indications of free ammonia in the exterior cell: the precipitated copper however did not exhibit the beautiful bright pink hue which it ordinarily presents, but was of a dull, greyish, earthy appearance, resembling that of copper over which ammoniacal gas has been passed at a red heat, and probably contained some combined nitrogen. I had not, however, time to examine a product which is worthy of further investigation.

I tried one more experiment with a view to complete the inquiry into the probable advantage of changing the battery charge. I placed a saturated solution of common salt in contact with the zinc, and filled the exterior division of the cells with a saturated aqueous solution of sulphate of copper. With a temperature of 70° the following series of observations was made:

Time.	Interval.	Voltameter.	5 min. rate.
h m	′	Cubic inches.	Cubic inches.
11 11			
11 15	4	3·5	4·3
11 19	8	5·9	3·
11 23	12	8·0	2·6
11 27	16	9·9	2·3
11 31	20	11·6	2·1
11 34			
11 54	20	4·	1·0

A fluid ounce of muriatic acid was added to each interior cell, and the action was only brought up to 2·7 cubic inches per five minutes. It thus appeared that the substitution of solutions of the muriates for dilute sulphuric acid, was in every way disadvantageous; and it was moreover found that when the circuit was broken the copper became seriously injured by their action and the formation of a submuriate of that metal.

Wishing now to extend the inquiry into the influence of high temperatures upon the voltaic current, and finding that the membranous tubes would not be able to resist the action of the acid under these circumstances, I endeavoured to find some substitute for the partition of the cells which would not be liable to injury from this cause. After several trials I found that porous earthenware, of the same texture as that of which wine coolers are commonly made, would answer my purpose sufficiently; and the arrangement which I ultimately adopted simplifies the construction of the battery to such a degree as to render it advantageous even under circumstances of ordinary temperature.

The interior cells consist of tubes of this earthenware, closed at the lower end, of the diameter of 1½ inches, and of the same height as the copper cells. The bottoms of the latter are fitted with sockets, in which the tubes are placed, and which confine them in their proper positions; the perforated copper plates, or colanders, for the reception of the solid sulphate of copper, pass over their upper ends. The tubes can be easily removed and instantly replaced; and the facility of emptying and refilling them renders the addition of syphon tubes unnecessary, except in very particular circumstances. Previously to their use they require to be thoroughly soaked in dilute acid; and I have not found them liable to injury, provided the sulphate of zinc be not allowed to crystallize within them; in which case they become disintegrated from the expansive force of crystallization. When the battery is out of action they may always be removed and emptied, and preserved in a state for immediate use by immersing them in very dilute acid. Liquid conduction is not carried on quite so perfectly through their substance as through the membranes, on account of the less perfect communication between the liquids on their opposite sides; but when the acid sulphate of copper is used the amount of action at ordinary temperatures is from 7 to 8 cubic inches per five minutes, which is quite sufficient for all ordinary purposes, and is moreover perfectly constant and steady.

Having thus prepared the battery, I caused a circular steam vessel to be made of tin plate, round which the cells could be placed upon blocks of wood, and closed in with a cover, in which there was a socket which could at pleasure be connected with the steam pipe of a boiler. Two other sockets were also conveniently placed, which were stopped with corks, through which the electrodes of the battery could pass, when the proper connections were made. I intended to have experimented with a series of ten cells, but owing to a mistake only nine could be conveniently arranged in the steamer.

The general result of numerous experiments was, that, the working rate of the battery having been ascertained at the ordinary atmospheric temperature, when steam was admitted it immediately began to rise; and at the full temperature of 212° was more than doubled, provided no *secondary action* interfered with it. The following series will be sufficient to illustrate the progress of the current: the temperatures were taken by a thermometer immersed in the steam.

Time.		Interval.	Voltameter.	5 min. rate.	Temperature.
h	m	′	Cubic inches.	Cubic inches.	°
10	0				
10	5	5	7·5	7·5	58
10	10	10	15·	7·5	58
			Steam admitted	. . . . .	110
10	25				
10	30	5	9·	9·	170
10	35	10	20·5	11·5	195
10	40	15	37·	16·5	200
10	41				
10	46	5	19·	19·	205
10	51	10	39·	20·	206

Wishing to ascertain whether any portion of this increased effect were owing to a simple increase of conducting power in the electrolyte, or whether it were wholly dependent upon the electro-motive force, or increased energy of affinity, I set the battery in action with a voltameter included in the circuit, the body of which was immersed in water, which could be conveniently raised to the boiling temperature by means of a lamp. The observations were commenced at the temperature of 58°.

Time.	Interval.	Voltameter.	5 min. rate.
h m	'	Cubic inches.	Cubic inches.
11 25			
11 30	5	6·5	6·5
11 35	10	13·	6·5
Voltameter heated to 130°.			
11 46			
11 51	5	6·5	6·5
Voltameter heated rapidly to 212°.			
11 56	10	14·	7·5
12 1	15	21·5	7·5
12 6	20	29·	7·5

The battery itself was then heated by steam to 135°.

Time.	Interval.	Voltameter.	5 min. rate.
h m	'	Cubic inches.	Cubic inches.
2 10			
2 15	5	13	13

A cell was then included in the circuit charged with cold standard acid, and without any sulphate of copper.

Time.	Interval.	Voltameter.	5 min. rate.
h m	'	Cubic inches.	Cubic inches.
2 20			
2 25	5	8	8
Cold cell removed.			
2 30	10	20	12
Cold cell restored with acid sulphate of copper.			
2 35	15	29·5	9·5

The temperature of the battery was then increased to 160°.

Time.	Interval.	Voltameter.	5 min. rate.
h m	'	Cubic inches.	Cubic inches.
2 38			
2 43	5	11	11
2 47	4	20·5	14

A small portion only of the increased effect would thus appear to depend upon the simple conducting power, which alone could have any influence in the voltameter with platinum electrodes; whilst the increased energy of the electro-motive force was checked by including in the circuit a cell whose powers had not been exalted by the increased temperature which had been communicated to the others.

At this period of my investigation some unexpected and highly interesting phenomena occurred, which turned out to be of a very complicated nature, and the unravelling of which cost me much time and labour. After careful consideration of the subject, I have come to the conclusion, that the clearest mode of giving you an account of these will be to adhere nearly to the order in which I followed them out.

In heating the battery in the steamer, it frequently happened (and indeed in the very first series of experiments which I made with it) that when the thermometer had nearly reached the boiling point, and the action of the battery was at its maximum, a sudden cessation would take place ; the decomposition of water in the voltameter, which was proceeding at the rate of 18 or 20 cubic inches per five minutes, would stop as suddenly as by the lifting of one of the connecting wires; and this suspension of power would continue for hours, provided the high temperature were maintained. Upon turning the steam off, and quickly cooling the steamer, the action would return as suddenly as it had ceased, though generally not to the full amount; falling mostly from about 20 cubic inches to 14 or 15. Upon turning the steam on, it would again stop, and again be renewed by cooling. Upon closely examining the voltameter upon these occasions, it was found that the current was not wholly stopped, but that there was a small residual action amounting to $\frac{1}{4}$ cubic inch per five minutes.

These experiments were often repeated with the same general results; and yet there were times when every care had been taken not to vary any of the circumstances of the arrangement, when they could not be reproduced.

In seeking for the cause of these phenomena, there were two which naturally suggested themselves as probable: the first was the unequal action of heat upon the different elements of the battery, exciting thermo-electric currents; and the second the possible excitement of opposing currents from the metallic steam case.

In heating and cooling the battery by the means which I have described, it is obvious that the temperature of its different parts would be unequally affected; and, in fact, I found by the thermometer that a difference of ten or twenty degrees would occasionally exist between the liquid in contact with the zinc and that in contact with the copper: these differences I attempted to increase and modify in numberless experiments. On one occasion I charged the battery with a cold acid solution of sulphate of copper on the outside, and poured boiling standard acid into the interior tube: the inequality did not long exist, but its action was steady at $8\frac{1}{2}$ cubic inches per five minutes. I heated the connecting wires to different degrees, and ultimately placed spirit-lamps under them, to maintain them at a low red heat; but the working rate of the battery, and its steadiness as measured by the voltameter, were not sensibly affected thereby. In short, I convinced myself, that though heat was obviously connected with the phenomena, heat alone was not their exciting cause.

With the view of ascertaining whether the residual current, after the sudden cessation of the greater action, were in the same direction as the original battery current, I included a galvanometer of a coarse construction, and consisting of a single large needle, in the circuit with the voltameter. I found that the needle was strongly deflected to the E., and that the deflection increased as the action rose with the rising temperature. Upon the sudden cessation of the action in the voltameter, the needle was suddenly released from its coercing force, and swang violently backwards and forwards W. and E. till it finally rested a few degrees to the W.; proving that the residual current which passed through the voltameter was in the opposite direction to the original current, and was the excess of a counter force which had power enough to arrest its course.

The cover of the steamer was now removed, and it was found that the bottom was covered with a considerable quantity of condensed water, which was slightly acid, from the leakage of one or two of the cells.

Upon taking out some of the connecting wires between the cells, some action still remained both upon the needle and voltameter, which was not wholly stopped till four wires were removed; proving the existence of a current in some circuit which was different from the main circuit of the battery.

I now tested the direction of the current in each separate cell of the battery, by leading extra wires from the zinc and copper to a second galvanometer, and found all in the normal direction (causing a permanent deflection of the needle 50° E.) except one, which presented a contrary current, and deflected the needle 30° W. Upon another occasion I found the current in six separate cells E., and three in the opposite direction, or W.; and once again one cell was found to be neutral, two reverse, and six direct. I proceeded to investigate with great care a phenomenon which promised at first to afford the explanation of the stoppage of the battery current. Let fig. 1. (Plate VIII.) represent the section of the voltaic combination : *a b c d* will be the steam-vessel, and the nine cells, with their connecting wires, will be represented by the nine smaller circles 1, 2, 3, 4, 5, 6, 7, 8, 9. In the experiment which I am about to describe, the electrodes *e* and *f* were unconnected, but all the short connecting wires were in their places. Each cell was tested by the galvanometer by means of extra wires, as at *g*. The cells 1, 2, 3, 4, 5, 6, 7, separately deflected the needle in the normal direction, or from 30° to 40° E. No. 8. deflected it in the opposite direction, or 40° W. The connexion between 8 and 9 was broken, and the same cell deflected the needle 35° E. The connection was then broken between 8 and 7, and the deflection was 30° E.; and when both wires were replaced, the needle returned to 40° W.

The whole circuit was then completed by the connection of 1 and 9 by a short wire, when, notwithstanding a path was open for the circulation of the battery current, the deflection caused by the single cell No. 8. increased to 55° W., which was contrary to the direction of the main circulation. While the circuit was thus complete, the other cells were again tested, with the following result:—

Fig. 1.

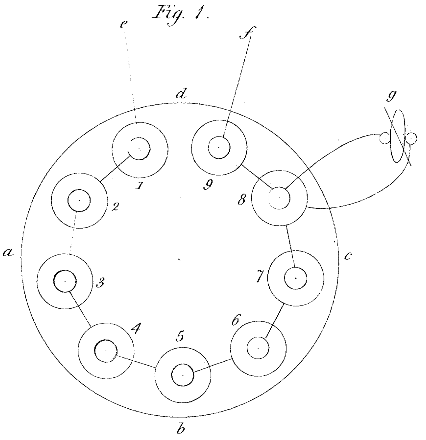


Fig. 2.

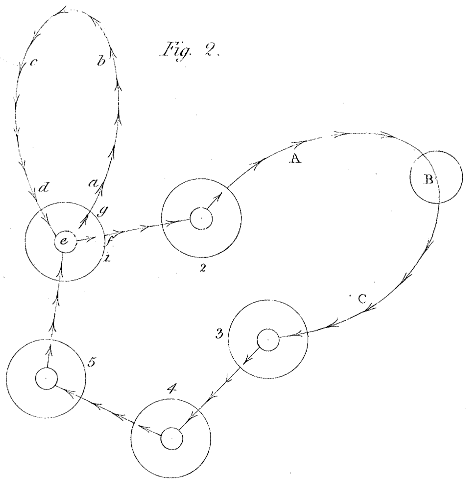


Fig. 3.

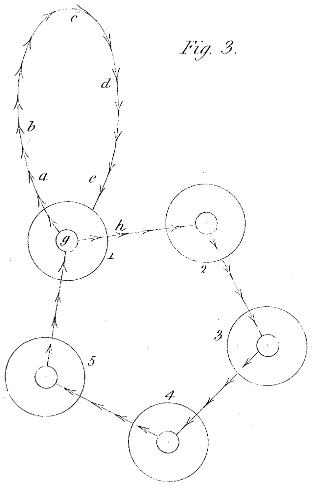


Fig. 5.

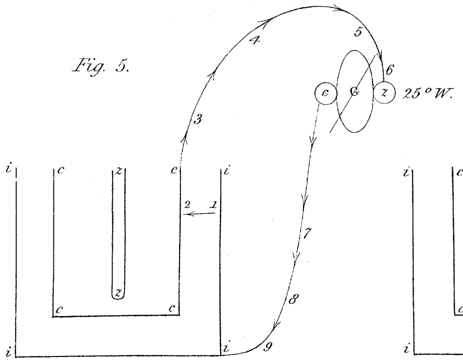


Fig. 6.

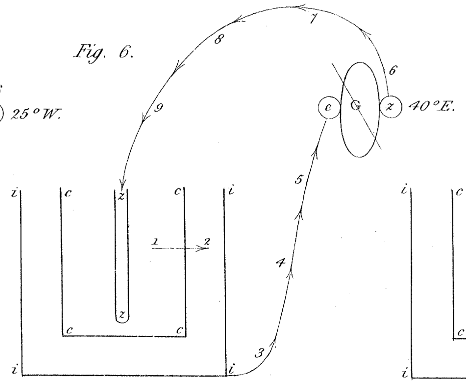


Fig. 7.

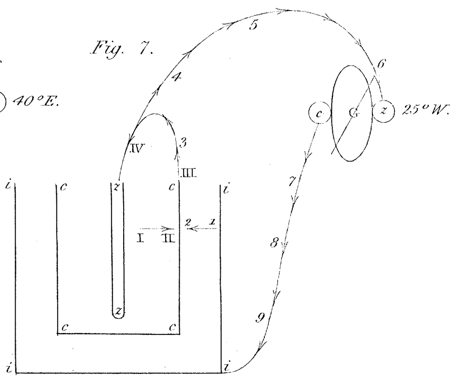


Fig. 4.

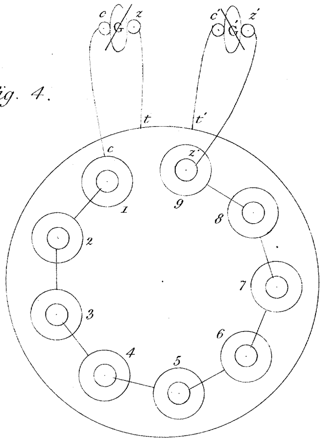


Fig. 8.

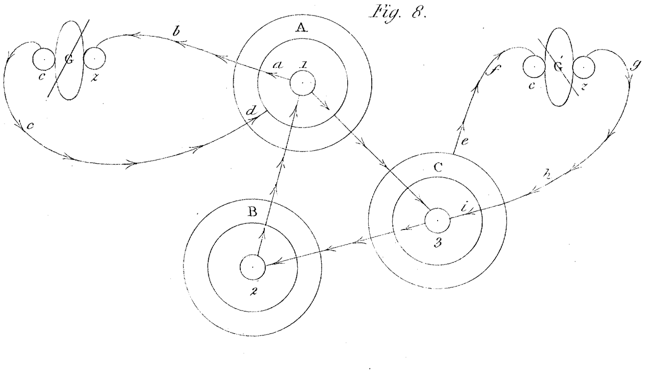


Fig. 9.

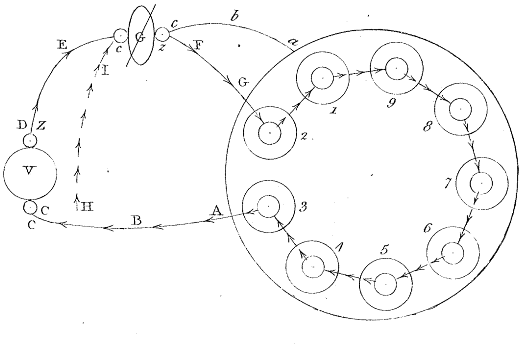
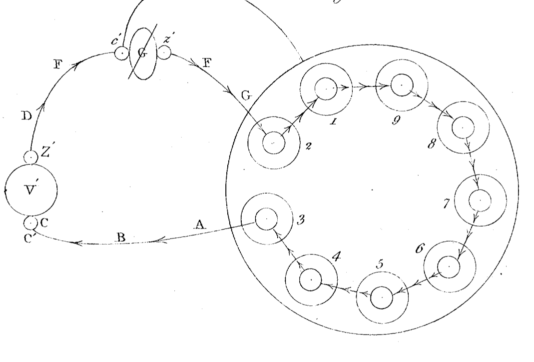


Fig. 10.



Js Basire sculp.

No. 8.—55° W.
7.—45 E.
6.—35 W.
5.—10 E.

With No. 4. the needle oscillated from one side of the coil to the other in the most extraördinary manner, first striking with considerable force against the pin on one side and then upon the other. Sometimes it seemed to hesitate between the two, and then to recede in one direction and advance in the opposite by sudden starts and jumps. These oscillations lasted for more than an hour, during which the experiment was continued, with equal force. The other cells were found,

No. 3.—10° W.
2.—20 E.

There was a strong spark upon breaking the connections of all these secondary currents, but they would not pass through the voltameter.

These experiments were frequently repeated with the same general results; sometimes a cell in one position indicating a reverse current, sometimes one in another, the same cell occasionally passing to the normal direction, and at times oscillating violently between the two.

To determine whether the metal steam-vessel had any influence upon these currents, five of the cells were removed to a table, and connected in series with a galvanometer, the needle of which was permanently deflected 90° E. When, in addition to the galvanometer connection, the two extreme cells were connected by a similar wire to those between the other cells, the needle was still deflected 15° E.: so that notwithstanding a shorter path was open to the battery current, and that through a conductor of considerably greater substance than the wires of the galvanometer, a portion still passed by the longer path. Under these circumstances, No. 1. cell was tested by a separate galvanometer, which was deflected 40° W. When the extra short connection of the battery was broken, the deflection from No. 1. fell to 30° W.; and when this cell was totally unconnected with the others, its current was in the normal direction, or 50° E. When the short connections were all restored, it again returned to 40° W. I must here observe, that the galvanometers, not being of the same construction, were not used as accurate measures of the force, but only to indicate the direction of the currents, and occasionally to show that the force was increasing or declining. The other cells were tested in the same way, with the following results:—

No. 2.	Battery connected by short wire . . .	30° E.
	Short connection broken . . .	55 E.
No. 3.	Battery connected	30 W. but changed to E.
	Unconnected	55 E.

No. 4.	Battery connected	20 E.
	Unconnected	50 E.
	Again connected	40 W.
	Again unconnected	50 E.
	Again connected	40 W.
	changed to 30° E.	
	and swang violently E. & W.	
No. 5.	Battery connected	35 E.
	Unconnected	55 E.
	Connected . oscillated E. & W.	30

Hence it appears that this variable current may be produced from the single cells of the battery, under ordinary circumstances, when the whole series is connected by short wires.

I was still desirous of ascertaining whether these currents would be produced in the simplest possible arrangement, viz. when the elements consisted of amalgamated zinc, copper, and dilute sulphuric acid. For this purpose the five cells were thoroughly cleaned, and charged entirely with standard acid, without sulphate of copper. They were connected in series with a voltameter, and each cell was separately tested by the galvanometer, with the following results:

Time.	Interval.	Voltameter.	5 min. rate.	Galvanometer.
1 56				
61	5	$1\frac{1}{4}$	$1\frac{3}{4}$	Cell 1.—45° E.
2 6	10	3	$1\frac{1}{4}$	Cell 2.—45 E.
11	15	4	1	Cell 3.—40 E.
16	20	$4\frac{3}{4}$	$0\frac{3}{4}$	Cell 4.—40 E.
21	25	$5\frac{1}{2}$	$0\frac{3}{4}$	Cell 5.—40 E.

The voltameter was removed, and the circuit completed by a short wire: the separate cells were again tested, with the following result:—

Cell 1.—25° E.
Cell 2.—20 W.
Cell 3.—20 W.
Cell 4.—25 W.
Cell 5.—25 E.

When the cells 2, 3, and 4, whose secondary currents were all W., or in the direction opposite to that of the main current, were all included in the secondary circuit, the deflection of the needle was 30° W.; but the current produced no decomposition in the voltameter when included with them. The deoxidation of the oxide of copper by the hydrogen was thus proved not to have been the exciting cause of the secondary currents.

I was now desirous of making a comparison of all these effects with the similar phenomena of the battery with its usual charge. The results of the latter are shown in the following Tables:

Time.	Interval.	Voltameter.	5 min. rate.	Galvanometer.
h m				
3 7				
3 12	5	5	5	Cell 1.—42½° E.
3 17	10	10	5	Cell 2.—45 E.
3 22	15	15	5	Cell 3.—45 E.
3 27	20	19½	4½	Cell 4.—47½ E.
3 32	25	24¼	4¾	Cell 5.—47½ E.

Circuit completed by short wire.

Cell 1.—25° W.
Cell 2.—30 W.
Cell 3.—30 W.
Cell 4.—30 E.
Cell 5.—30 E.

The assisting action of the sulphate of copper was thus found to have increased the decomposing power of the battery current from 1·1 cubic inch to 5 cubic inches, and the force of the secondary current, as measured by the deviation of the galvanometer, from 40° to 47°.

From these experiments we find that when the course of the main battery current is obstructed by causing it to pass through the long wire of a galvanometer, or through the electrolyte of a voltameter, the course of the secondary current from each separate cell is always normal, or in the same direction; but that when the battery current is allowed to flow with the least possible resistance, as by completing the main circuit by a short wire, the secondary current of the separate cells becomes opposite. Hence it might be inferred that the resistance might be so adjusted as that the secondary current should altogether disappear, or vary between the two directions. To ascertain the effect of different degrees of resistance, the following experiments were made.

A galvanometer was included in the main circuit of the battery, formed of a wire one twentieth of an inch in diameter and thirty-two feet in length: this we will designate as No. 1. An extra connection was also made of the circuit by means of a wire of the same thickness, fifty-three feet four inches long. The diameter of the wire forming the battery connections was one seventh of an inch. A secondary circuit was also formed from a single cell through another galvanometer, which we will call No. 2.

The deviation of No. 1. was 70° E.
No. 2. — 40 E.

and both the needles were perfectly steady.

When the extra connection was reduced to half, or twenty-six feet eight inches,

The deviation of No. 1. was 60° E.
No. 2. — 35 E.

and No. 2. wavered a little.

Extra connection again halved, or thirteen feet four inches,

The deviation of No. 1. was 40° E.
No. 2. — 30 E.

and No. 2. began to oscillate.

Extra connection once more halved, or six feet eight inches,

The deviation of No. 1. was 28° E.

and No. 2. oscillated from E. and W. very strongly.

The extra connection was then made by only four inches of the same wire:

The deviation of No. 1. was 15° E.
No. 2. — 30 W.

and the needle was only slightly unsteady.

The extra connection was then entirely removed, and

The deviation of No. 1. was 80° E.
No. 2. — 45 E.

Now with regard to the main battery current, when the extra connection was wholly removed, the whole passed through No. 1. galvanometer with a certain resistance, and was measured by its deflection 80°: when the long wire was added, a portion was diverted into the new channel, and was measured by the decline of the needle to 70°. As the length of the extra wire was shortened, the resistance of this passage decreased, and more and more of the current was diverted from the galvanometer till the deflection of the needle only amounted to 15°, and nearly the whole passed through the extra wire.

The effect of these varying resistances upon the secondary current I think I can explain with the help of the annexed diagram. Let the circles 1, 2, 3, 4, 5, (fig. 2.) represent sections of the five battery cells, and the lines between 3 and 4, 4 and 5, 5 and 1, and 1 and 2, with the arrow heads, the short wires between the zinc of each cell and the copper of the next, with the direction of that conventional current which is supposed to flow from one to the other. Let A B C represent the long wire of a galvanometer, or the electrodes of a voltameter through which the circuit is completed between 2 and 3, and by which the current is resisted. When a secondary connection is formed by the wire *a b c d*, between the zinc *e* and the copper *g* of the cell No. 1, a portion of the main current, which tends to pass through the electrolyte to the copper at *f*, being obstructed in this direction, passes to *g*, and completes its circuit through the wire *a b c d*, and the *diverted current* obviously will flow in the same direction as the main current, or from the copper through the wire to the zinc.

But if, instead of a resisting communication, the primary circuit be completed between 2 and 3 by a short wire, as between the other cells, and as represented at fig. 3., and a secondary circuit be formed as before with the cell No. 1. by the wire *a b c d e*, a portion of the main current flowing from the copper of No. 5. to the zinc of No. 1, instead of passing through the electrolyte from *g* to *h*, finds a passage through the wire *a b c d e* to *h*, and consequently will appear to flow in an opposite direction to the primary current or from the zinc to the copper. The resistance of the circuits may be so adjusted that the current may sometimes take one course and sometimes the opposite, and produce those oscillations of the needle from E. to W. which have been just described.

The breaking of the secondary circuit did not affect the galvanometer of the primary current, but the breaking of the primary circuit always turned the secondary current into the normal direction, and increased the deviation of its needle; it reduced it, in fact, to the condition of the direct current from the single cell.

It is however obvious that these *diverted* currents of the complete circuit would not of themselves be sufficient to account for the stoppage of the main battery current of which we are in search; nor has it yet been shown how they were produced when the main circuit was broken, as represented at fig. 1. In search of the explanation of these phenomena I turned my attention to the influence of the metallic steam-vessel upon the voltaic arrangement.

When the battery was connected in the usual way with a galvanometer, and the needle was deflected 80° E., if the zinc electrode were lifted and made to touch the tin case in any part, it would remain deflected in the same direction 30°. If, on the other hand, the main circuit were broken at the copper electrode, and it were brought into contact with the tin, the deflection would be to the same amount in the same direction. The difference of that connection is shown at fig. 4, where *t z* represents the zinc electrode in connection with the tin, and passing to the zinc cup of the galvanometer G and the copper electrode C C in its usual position. On the other hand, z' z' represents the zinc electrode in its usual communication with the galvanometer, and the copper electrode c' t' in connection with the tin. The most striking result of this experiment is, that notwithstanding the connection of the tin with the galvanometer is reversed, the current is in the same direction; or that the current, which we must conceive to flow from the tin in one connection, must flow to the tin in the other. To simplify the conditions of the experiment, I repeated it with a single cell. At the atmospheric temperature of 52°, when the circuit was completed in the usual way through the galvanometer, the deflection was 57° E.; but no deflection was obtained by making connection with the tin. When steam was admitted, the ordinary battery current increased to 65°, and then contact with the hot tin produced a deflection of 20° E. by either electrode.

Four cells were now placed in the steam case upon plates of glass, and the action of the battery with the usual connections being first tried at the temperature of 54°, was found as follows:

Galvanometer alone	70° E.
Galvanometer with voltameter . . .	50° E.

Voltameter alone	5 cubic inches per five minutes.
Voltameter with galvanometer	4 cubic inches per five minutes.

At this temperature there was no current from the tin by either connection.

When the steam was turned on, the battery current increased rapidly to 85° E. by the galvanometer, and there was a current from the tin connections notwithstanding the glass insulation. This *extra current* was also found to exist during the flow of the main battery current; and when the two were measured by separate galvanometers,

The battery current was	85° E.
And the extra current	30 E.

It again made no difference whether the tin took the place of the zinc or the copper in the arrangement; the deflection was always in the same direction.

The breaking of neither current affected the other.

To ascertain whether heat alone, independent of the steam, was the cause of this extra current, a tin plate was placed upon the hot sand of a sand-bath, and the battery cells transferred to glass plates upon it. At first no extra current was detected; but as the temperature rose to 150° and 200°, the second galvanometer was affected to the amount of 50° or 60°; and this whether the battery circuit was complete or not. A deflection was even occasioned by making the contact with any part of the iron stove, however distant, with which the tin plate was in contact.

These experiments were repeated and varied numberless times, but not with uniform results: sometimes the extra current had sufficient intensity to pass through a voltameter, producing slow decomposition of the water; but most frequently, however great the deflection of the needle, it would not pass through this obstacle. At other times, in apparently similar circumstances, the extra current could not be detected at all. Whenever produced, however, it was always observed to flow from the tin to the battery, whether the connection with the latter were made with the zinc or the copper.

I now placed one of the battery cells upon a piece of wood in an iron case made to receive it, of the same height, but having a space all round it of about an inch. When the primary circuit was completed by means of a galvanometer, the deflection was 60° E.; but there was no action upon a second galvanometer included in a secondary circuit between the iron and the zinc or the iron, and the copper of the cell. A little dilute sulphuric acid was then poured into the iron case, and immediately a strong extra current was produced. Under these circumstances

The primary current was	60° E.
The extra current copper and iron connection	20 E.
Zinc and iron	40 E.

The analysis of the phenomena of these extra currents was most satisfactorily performed in the following manner:—in figg. 5, 6, and 7, let *i i i i* represent the section of the iron case, *c c c c* the section of the copper cell, and *z z* the zinc rod: let G also represent the situation of the secondary galvanometer with its different connections with the circuit. In fig. 5. the connection with the iron is made with the copper cup of the galvanometer, and the zinc cup is connected with the copper of the cell; and we see at once that a current is established, which, setting out from the iron, passes through the electrolyte to the copper, and completes its circuit through the galvanometer in the direction 1, 2, 3, 4, 5, 6, 7, 8, 9. In fig. 6. the connection with the iron remaining the same, the battery cell is connected by its zinc rod with the zinc cup of the galvanometer, and we have a powerful reversed current, which we must suppose to set out from the zinc, and to pass through a portion of the electrolyte to the copper, and from the copper through another portion of electrolyte to the iron, and to complete its course in the direction 1, 2, 3, 4, 5, 6, 7, 8, 9. In fig. 7. the main battery circuit is likewise completed, and the primary current will flow in the direction I., II., III., IV.; while the extra circuit, although apparently connected, as in fig. 6, with the zinc, is in fact connected with the copper, as in fig. 5, by means of the main battery connection, and will convey the extra current from the iron through the electrolyte to the copper, and from the copper through the galvanometer back again to the iron in the direction 1, 2, 3, 4, 5, 6, 7, 8, 9.

It will be seen that the two currents coincide in their direction in that part of their circuits which is common to both, viz. III., IV., and 3, 4.

There is no difficulty at all in understanding how an extra current is established from the iron to the copper in addition to the main current from the zinc to the copper; but I was for a long time puzzled to make out how an extra current could pass from the zinc through the electrolyte to the copper, and from the copper through the electrolyte to the iron: it seemed to me that the interposed copper must act as a retarding plate, upon the opposite surfaces of which hydrogen and oxygen must be evolved; and that the intensity of a single circle could not be sufficient to force this passage. You will, I dare say, remember suggesting an experiment which led to the explanation of the difficulty.

Some dilute sulphuric acid was poured into a basin, and a platinum crucible containing some solution of sulphate of copper was placed in it. An amalgamated zinc rod wrapped in filtering paper moistened with dilute acid, to prevent it from precipitating the copper by its local action, was held in the crucible. A plate of iron was also immersed in the acid in the basin; contact with the platinum being carefully avoided. A metallic communication was then made by means of a wire with the zinc and the iron, and we had thus the exact circumstances of the battery cell in the iron case, except that platinum was substituted for copper. No current, however, was thus formed, and no copper was precipitated upon the platinum from the solution of sulphate. A piece of copper-plate was now placed under the platinum crucible, and in contact with it: the current immediately passed, and copper was precipitated upon the interior surface of the crucible from the sulphate. The current of the single circle could not pass by the retarding plate of platina, when oxygen must have been evolved on one side and hydrogen on the other; but when the oxygen was absorbed by the copper, and the hydrogen by the oxide of copper, these concurring affinities enabled the current affinity to make good its circuit.

To vary the experiment with regard to the metallic part of the combination, three of the battery cells were placed upon zinc plates with interposed flannel moistened with dilute sulphuric acid; the copper was thus placed between two generating plates of the same metal. When the three were connected together in regular series with a galvanometer, the deflection of the needle was 90° E. When a secondary connection was made from the zinc rod of each cell in succession through another galvanometer with the zinc plate on which it stood, the deflection occasioned by the extra current was 20° W. In this case it must have flowed from the zinc through the electrolyte in the flannel to the copper; from the copper through the electrolyte in the cell to the zinc rod; and from the zinc rod through the wire back to the zinc plate. When the main circuit was broken the extra current changed its direction, and occasioned a deflection of the needle 20° E. Upon restoring the primary current the extra current again returned to its original direction, and so invariably upon many successive repetitions of the experiment.

When the extra connection was made between the copper of the cell and the zinc plate, the deflection of the second galvanometer was always 40° W., or opposite to the main current, and was not disturbed by any interruption of the latter.

Being now satisfied that these extra currents were hydro-electric, and dependent upon the action of a liquid upon the metal which was brought into association with the regular voltaic combination, I examined more carefully the circumstances of the arrangement in which I had supposed that I had insulated the cells, and cut them off from any such influence by placing them upon thick glass plates. I now ascertained that the establishment of the extra current was owing to a thin film of moisture formed upon the glass, either by the condensation of steam, or slight leakage from the cells. At ordinary temperatures no action was thus excited, but when the temperature of the combination was sufficiently exalted very energetic currents were sometimes developed by a quantity of moisture, which might well have escaped ordinary observation. When great care was taken to make the glass plates perfectly bright and dry, the extra current was never produced.

It was now also clear that not only could independent extra currents be established, but that different portions of the main battery current could be diverted into this secondary path, and thus the occasional decomposition of water in the voltameter by the extra current could be accounted for.

There is one more relation of the *battery current*, the *diverted current* and the *extra current*, which it may be worth while to point out when they are all three established at the same moment. Let 1, 2, 3 (fig. 8) represent the section of three battery cells, all standing upon blocks of wood in iron cases, the sections of which are represented by A, B, C, the bottoms of the cases being covered with dilute acid. The main connections of the battery are made, and the principal current flows from 1 to 3, from 3 to 2, from 2 to 1. A diverted current may be led off from 1, and may pass in the direction *a b c d* through the galvanometer G, or sometimes in the opposite direction. At the same time an extra current may be established from C, the iron case of the cell 3, through the galvanometer G′, in the direction *e f g h i*.

The making or breaking of this extra current had no effect upon the diverted current *a b c d*, but the two were always in opposite directions. When the first moved the needle to the E. the second deflected its needle W. When the diverted current was W. the breaking the main current always turned it in the normal direction E, and at the same moment the needle of the extra current changed to the W. Upon restoring the main current both needles returned to their former position.

When the battery current, instead of being allowed to flow through short connections, was led through a separate galvanometer, each of the other currents passing also to separate galvanometers, the diverted current varied in the different cells from 45° to 20°, but was always in the normal direction, and the extra current was opposite. When the short connection was added to the battery, as well as the long one through the galvanometer, the latter fell from 90° E. to about 20° E., and the diverted current oscillated rapidly E. and W., and the needle of the extra current changed with it in the opposite directions W. and E.

I could now have no doubt that the explanation of the sudden stoppage and reversal of the battery current, of which I was in search, was to be found either in this diversion which I have described, or from the opposition of extra currents exalted in their power by heat, or possibly from some combination of the two. I therefore returned to the original combination of the battery in the steamer.

I soon ascertained that the extra current could be produced by a connection from any part of the tin case to any of the cells of the battery standing upon wooden blocks, and that its energy was increased both by acidulating the condensed water and by heat. I found also that by leading this current through the same galvanometer and voltameter as the battery current, that it interfered with it in different degrees, even to its stoppage and reversal. I must not attempt to give you the details of the numerous series of observations which I have made upon the subject, but will content myself with stating as concisely as possible the results of the last combination, which have proved always constant.

At figg. 9 and 10 I have represented, as before, a section of the arrangement: the course of the main current is marked by the arrow heads, and is conducted by the electrodes through the voltameter V and the galvanometer G. The battery was first charged in the usual way, and the cells were placed in the steamer upon blocks of damp wood standing in a little acidulated water. The observation commenced at the temperature of 52°, and the following are the tabulated results.

Time.		Interval.	Voltameter.	5 min. rate.	Galvanometer.
h	m	′	Cubic inches.	Cubic inches.	°
10	58				
11	3	5	6	6	60 E.
11	5				
11	10	5	12	6	60 E.

A connection was now made between the tin and the zinc cup of the galvanometer, as in fig. 9, by *a b c*, and the action was decreased.

Time.	Interval.	Voltameter.	5 min. rate.	Galvanometer.
h m	′	Cubic inches.	Cubic inches.	°
11 11				
11 16	5	17·	5	55 E.
11 21	5	21¼	4¼	

The cover of the steamer was next put on, and the connections made as before by the electrodes passing through the cocks.

Time.	Interval.	Voltameter.	5 min. rate.	Galvanometer.
h m	′	Cubic inches.	Cubic inches.	°
11 40				
11 45	5	6·5	6·5	60 E.

Connection was again made from the tin (cover) to the zinc cup.

Time.	Interval.	Voltameter.	5 min. rate.	Galvanometer.
h m	′	Cubic inches.	Cubic inches.	°
11 50	5	11·5	5·	55 E.
11 52	The steam was turned on.			
11 57	5	19·	7·5	65 E.
12 2	5	27·	8·	67·5 E.
12 7	5	36·	9·	70 E.
12 9				
12 14	5	11·	11·	77 E.
12 19	5	21·5	10·5	

The tin was again connected as before.

Time.	Interval.	Voltameter.	5 min. rate.	Galvanometer.
h m	′	Cubic inches.	Cubic inches.	°
12 24	5	25·	3·5	40 E.
12 29	5	stopped.		0

Now we may observe that in this arrangement the extra current, which we have already found completing its circuit, according to circumstances, either to the zinc or copper of the battery, has a path open to it by the wire F G to the zinc of No. 2, or through the galvanometer and voltameter by the wire B A to the copper of No. 3, the latter being in opposition to the battery current. That in this series of experiments it tended to pass in the latter direction, is proved by the gradual retardation and ultimate neutralization of the latter. When the resistance to the main current was diminished by throwing the voltameter V out of the circuit by a wire passing from H to I, it again passed in the regular course, turning the needle of the galvanometer to the E.

When the secondary connection was made with the tin by the copper cup C of the galvanometer, instead of the zinc cup, the battery current through the voltameter was again stopped, but the needle of the galvanometer turned 80° E., indicating a powerful current through it in the normal direction.

These experiments were frequently repeated with the same results.

In attempting to account for all the variable phenomena of these extra and diverted currents, it must not be overlooked that it may be possible for the whole battery, or for a certain number of the series of the battery, to force itself a passage through the electrolyte on each side of the copper to the tin, and thus to discharge itself by what would appear to be a reversed current through the secondary communication. This would be determined by the amount of different resistances in the paths which might be open to it. In this way we can account for the different degrees of power in the extra current, and for its being able to pass through the voltameter at times and not at others.

The only difficulty in now accounting for the original stoppage of the battery current which I observed, consists in my not having been aware that there was any metallic communication between the tin and any of the battery connections. I am now however convinced that, notwithstanding precautions were taken to avoid this, contact must have taken place. Indeed the distance between the connecting wires and the rim of the tin cover was but small, and the jarring occasioned by placing the cover in its place may easily have occasioned sufficient disturbance in the arrangement. This supposition also sufficiently explains why the stoppage could not invariably be produced when desired.

I think that I do not deceive myself in believing that the preceding observations may not be without interest and importance to those who are actively engaged in advancing by experiment our knowledge of one of the most wonderful and widely-diffused agencies with which matter has been endowed. If they should answer no higher purpose, they may very probably prevent the application of much labour and thought in the explanation of phenomena of a very striking but perplexing nature, which are very likely to be observed by those who are working in this field of inquiry, and of which in my own case the preceding pages are a very brief abstract. At the same time they afford an exemplification of the advantages of the *constant battery*; for both the diverted currents and the effects of temperature would have been masked and lost in the variable results of the common voltaic combinations.

The effects of heat upon single voltaic circuits have been ably investigated both by M. Marianini* and by Mr. Rogers†; but although both these gentlemen purposed to extend their observations to compound circuits, or the battery, they have probably been prevented by the cause which I have indicated. It is now, however, apparent that in the exact measures of different effects which an invariable current of electricity will enable experimentalists to undertake, the variations of atmospheric temperature even must not be neglected.

I remain, my dear Faraday,

Yours very faithfully,

J. F. Daniell.

King's College,
March, 1837.

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* Annales de Chimie, tom. xxxiii. p. 132.

† Silliman's Journal, January, 1835.

POSTSCRIPT.

I have just completed a *constant battery* of large dimensions, the effects of which exceed my most sanguine expectations, and open new views of the possible application of the extraordinary powers of the voltaic current to economical purposes. It consists of only ten copper cells 20 inches high, $3\frac{1}{2}$ inches diameter, as in the first battery. The interior partitions are formed by merely tying the open ends of the oxen's gullets to the rings of the colanders for supporting the sulphate of copper, and which are made deeper than before, and suspending them in the cells, to the bottoms of which they reach. These membranous bags contain each rather more than a quart of the dilute acid. The zinc rods are of the diameter of $\frac{5}{8}$th of an inch, well amalgamated, and the connections are made as before described. At the temperature of 67° this battery produces, in the voltameters which I have all along employed in these researches, 12 cubic inches of the mixed gases per minute, or 720 cubic inches per hour. Its powers of ignition are very great; and while it will maintain 6 inches of platinum wire $\frac{1}{100}$th of an inch diameter red hot, it will still decompose water at the rate of 14 cubic inches per five minutes. The permanence of this result is very striking.

When the battery is not in use the rods are taken out and wiped, and the membranous bags carefully lifted out of the cells, emptied of their acid, filled with water, and suspended from a frame placed for their reception. By this treatment I do not find that they are liable to any change of texture or deterioration; and I have now membranes which have been in use for several months and are quite perfect. If the acid be perfectly washed out of them they may even be dried with impunity; but it is better to preserve them in a moist state, as when dry they are liable to crack. The acid solution of sulphate of copper remains in the cells without injury, and in ten minutes the battery, when required, may be brought into action. There is no reason to think that the limits of efficiency have yet been nearly attained, and the gullets could easily be connected together so as to obtain bags of any required length. I scarcely, however, think that in simplicity and cheapness of construction the battery can be further improved.

J. F. D.

King's College,
15th June, 1837.