PHILOSOPHICAL TRANSACTIONS.

VIII. *Sixth Letter on Voltaic Combinations. Addressed to* Michael Faraday, *Esq., D.C.L. F.R.S., Fullerian Prof. Chem. Royal Institution, &c. &c. &c.*

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My dear Faraday,

I MUST beg permission to address you once more upon the subject of Voltaic Combinations. To this I am prompted by several considerations.

In the first place, the beautiful law of Ohm, and the simple expression which he has given of the electromotive force and resistances of a voltaic circuit, enable me to review with advantage, and to correct, many of the conclusions which I had derived from former experiments; and have suggested additional experiments, the results of which will tend, I trust, to remove some obscurities and ambiguities which were left in my former communications.

2nd. By following out these principles I shall be enabled to offer some practical remarks upon the different forms of voltaic batteries which have been brought forward to assist the speculations of the active inquirers, who, in the present day, are so eagerly engaged in applying the voltaic forces to the service of the arts.

3rd. I wish most particularly to explain more fully the principles of the cylindrical arrangements of the battery which I have introduced, and which appear to me to have been greatly misunderstood.

I am desirous, however, that you should understand that I do not present the following observations for the purpose of testing the law in question, or of determining constants connected with the formula, for that could only be satisfactorily effected by experiments of a much more delicate and accurate nature than those to which I shall have to refer; but with a view to show how generally the law applies, even to the practical results of operations carried on upon, what might be called, a manufacturing scale, in which disturbing influences are numerous, and in a great measure uncontrolable.

Professor Ohm has adopted (I believe that you will concur with me in thinking, unfortunately) the contact theory of the electromotive force; and although his *formula* is easily adapted to either of the two rival views, it is perhaps necessary, in selecting the chemical theory, that I should define the exact meaning which I attach to his symbols, and explain the expansions which I think it necessary to introduce. The formula, you will remember, is

$$\frac{E}{R+r}=A,$$

where E represents the electromotive force (so called) in the cell: R the resistances in the cell: r the amount of exterior resistances: A the effective force, measured by the work performed. Now according to the chemical view, E must be the balance of several active forces in the cell.

1st. The superior affinity of the *generating* plate for the *anion*, of the electrolyte, which we will designate by B.

2nd. The inferior affinity of the *conducting* plate for the same *anion*, which we will call b.

3rd. The affinity of the *cation*, disengaged from the electrolyte and accumulated upon the conducting plate for the *anion*, this we will call e': these two last tend to produce polarization, as it is not very appropriately called, and a current in the opposite direction to B; therefore

$$E=B-(b+e'),\text{ or}$$
$$E=B-b-e'.$$

R, the resistance in the cell, varies *directly* as the thickness of the electrolyte (or the distance between the generating and conducting plates), D, and inversely as the area of the section of the electrolyte, S; therefore

$$R=\frac{D}{S}*.$$

r represents all the exterior resistances, whether metallic or electrolytic. In the metallic parts of the circuit, it will be *inversely* as the area of the section (*i. e.* the square of the diameter) of the wire s, and directly as the length l, or distance through which the current passes. In electrolytic work this metallic resistance may generally be disregarded; the lengths of the connecting wires being insignificant with regard to the resistance of the electrolyte. This latter will be inversely as the area of the section of the electrolyte, s', and *directly* as the distance d between the electrodes: therefore

$$r=\frac{l}{s}+\frac{d}{s'}.$$

But we must now inquire particularly what it is we mean by the section of the electrolyte. The limits of the section of the metallic conductor are strict and easily

* The resistance of each liquid is specific, and depends upon the nature of the liquid, the degree of saturation (if a solution), and the temperature; these circumstances remaining constant, it also is constant, and is so considered in this review of the formula.

determined; but, taking into consideration the diffusive nature of the electrolytic force, and the wide spread of that polarization of the particles of an electrolyte which we have traced upon a former occasion to the back surface of a conducting plate opposed to a mere point of generating metal*, it is more difficult to define the limits of its action so as to satisfy the conditions of the *formula*.

In a cell composed of a plate of generating metal with a conducting plate of equal dimensions, the interposed electrolyte only wetting the opposite faces of the two metals, the area of the section of the electrolyte will clearly be equal to the area of the acting surface of the conducting plate. In case the two metals should be immersed in a trough, in such a manner as to allow of the electrolyte being in contact with both sides of the plates, it is also probable that the action of the back surfaces might be disregarded without danger of material error in our calculations, although we know in fact that they would not be wholly passive. Up to this point, therefore, there is no difficulty in the application of OHM's formula.

But how are we to determine the area of the section of the electrolyte, when the surfaces of the generating and conducting plates are not equal? as, for instance, in the case of a rod of zinc placed within a cylinder of copper. Is it referrible solely to the surface of the conducting plate? Or is it limited by the mean of the surfaces of the two plates? The experimental investigation of this point, although the final result is extremely simple, has cost me much labour. The apparently unlimited spread or radiation of the force from a point of generating metal over an indefinitely large surface of conducting metal, strongly suggested the first conclusion. This was moreover confirmed by the following consideration, viz. if we take the mean section of the electrolyte as determined by the mean of the surfaces of the two metallic plates between which it is included, it is clear that the result ought to be the same, whether the generating or conducting metal be the larger of the two. A rod of copper placed within a cylinder of zinc, ought to circulate the same amount of force as a rod of zinc placed within a cylinder of copper; the dimensions in both cases being respectively the same.

Now the results of a vast number of experiments, some of which I have already submitted to you†, seemed to prove that, so far from this being the case, the amount of force is reduced one-half when the lines of force are made to converge from a large generating surface towards a small conducting one; instead of diverging in the contrary arrangement, from a small generator to a large conductor.

These experiments I have again repeated, and when I made use of sulphate of copper in dilute sulphuric acid as the electrolyte, with the same general results.

The impossibility of reconciling this with the law, and the necessity of determining a point of such fundamental importance, together with a certain degree of unsteadiness of action in the experiments, induced me, at length, to change the electrolyte for one which would be less liable to alter its condition during the progress of the

* Philosophical Transactions, 1838, Part I. p. 54.

† Ibid., pp. 47, 49, 53.

observations. The arrangement which I adopted was that of hollow cylinders of amalgamated zinc with platinum wire, and wire of amalgamated zinc with platinum cylinders, all of equal heights ; and the electrolyte in contact with the zinc consisted of standard dilute sulphuric acid, separated by a porous tube from strong nitric acid in contact with the platinum. A BREGUET's thermometer, adapted to the purposes of a galvanometer*, was selected as a measure of the effects. The following Table exhibits the results :—

TABLE I.

Diameter of Zinc.	Diameter of Platinum.	Degrees of Galvanometer.
inches.		
$2\frac{3}{4}$	wire	274° Mean of three observations.
wire	$2\frac{3}{4}$	255 Mean of three observations.
wire	$1\frac{1}{3}$	279
$1\frac{1}{3}$	wire	273
		270 Mean.

The needle always returned after each experiment to the point from which it started. There can be no difficulty in taking these results as sensibly equal; and it is therefore evident that a wire of platinum placed within a cylinder of zinc, established a current of exactly the same force, as a wire of zinc placed within a cylinder of platinum of equal diameter. Hence we may conclude that the area of the efficient section of the electrolyte is the mean of the opposed faces of the metal plates.

But how shall we account for the contrary results with sulphate of copper as the electrolyte, which were carefully made and greatly varied, but which always gave a consistent result of about one-half the force when the conducting was very small in proportion to the generating surface?

By substituting acid sulphate of copper for nitric acid in the arrangement just described, and carefully attending to the progress of the experiment, the explanation became obvious.

When the platinum wire was placed in the porous tube in the centre of the zinc cylinder, upon first connection with the calorific galvanometer, the needle advanced to 83° ; but almost immediately began to return till it reached 28°, at which point it remained stationary. When the wire was withdrawn it was found covered with copper in a spongy or pulverulent form. It was wiped and replaced, and the needle advanced to 85°, but immediately began to retrograde and fell again to 28°. This process was repeated many times, and always with the same result. If, while the galvanometer was at its highest point, the wire was moved about and the liquid kept in a state of agitation, the needle remained steady for a longer time; but when the wire was left at rest, the needle always receded.

* Philosophical Transactions, 1838, p. 42. This instrument is not absolutely to be depended upon when the power is high and the differences to be measured great, on account of the differences in its rates of cooling.

When, on the contrary, a zinc wire was placed in the porous tube in the centre of the platinum cylinder, charged with the sulphate of copper, the needle advanced to 96° upon an average of three experiments, and then remained quite steady. In this case, the precipitated copper was equally diffused over the surface of the platinum, and constituted a compact layer firmly attached to the plate. There can be no doubt that it is this difference in the state of the precipitated metal which gave rise to the difference in the results of the two arrangements. In the last case, the electrolysis of the liquid was carried on without the disengagement of any element tending materially to produce an opposing current; while in the first, the spongy state of the copper retained the liquid within its pores; which, after the precipitation of all the sulphate of copper which it contained, generated hydrogen, which was equally entangled in it, and produced a strong opposition to the current. The amount of this opposition is definite, and of nearly half the force of the principal current; and hence I was led to the erroneous conclusion regarding the relative sizes of the generating and conducting plates. Taking the measure of the force at the first moment of making the contacts, the results sufficiently confirm the conclusion drawn from the experiments with the nitric acid.

I once more tested the hypothesis, that it is the mean section of the electrolyte which regulates the current, and that it is indifferent whether the conducting or the generating metal be the larger of the two plates, by measuring the chemical results produced. For this purpose I weighed the amalgamated zinc cylinders and rods before and after the experiment, and ascertained the consumption of metal for intervals of half an hour, during which the circuits were closed. The conducting metal was copper, and the rods half an inch in diameter. The electrolyte was sulphate of copper and dilute sulphuric acid, and was kept agitated during the immersion of the copper rods. The results are set down in the following Table:—

Table II.

Diameter of Zinc.	Diameter of Copper.	Loss of Zinc in thirty minutes.
inches.	inches.	grs.
$\frac{1}{2}$	$2\frac{3}{4}$	30
$2\frac{3}{4}$	$\frac{1}{2}$	30
$\frac{1}{2}$	$5\frac{1}{2}$	29·7
$5\frac{1}{2}$	$\frac{1}{2}$	30

These results perfectly accord with the preceding.

From the consideration of the foregoing experiments, we are led to another important relation of the generating and conducting metals in these cylindrical arrangements, to understand which, it must be borne in mind that the surfaces of cylinders, of equal heights, are directly proportioned to their radii.

Let us therefore imagine an indefinitely small rod of a generating metal placed in the axis of a cylinder of conducting metal of a given diameter, filled with an electrolyte; upon making contact of the two metals, a current would be established of a definite amount. The area of the mean section of the electrolyte would be the area of a cylinder placed half way between the cylinder and its axis, or half that of the cylinder; and it would be the same whether the generating or the conducting metal were the exterior of the two.

Now the amount of the current ought to be the same whatever might be the diameter of the exterior cylinder, for the resistance occasioned by increasing the depth of the electrolyte, that is to say, by increasing the radius of the cylinder, is exactly counterbalanced by the increased conducting power conferred by the increased area of the section of the electrolyte, and *vice versâ*. The results of the experiments confirm this conclusion; for upon reference to Table I. it will be seen that cylinders of $1\frac{1}{3}$ inch and $2\frac{3}{4}$ inches diameter produced, under like circumstances, the same amount of current; and from Table II. we learn that cylinders of $2\frac{3}{4}$ inches and $5\frac{1}{2}$ inches diameter had equal influences.

You may perhaps remember, that in my former communications, from some experiments upon this point*, I had obtained some anomalous results which occasioned me considerable perplexity, but I have since multiplied observations sufficiently to place the confirmation of the law beyond a doubt.

Amongst others, I repeated the experiments with the large battery of ten cells of four inches diameter, in comparison with ten of $3\frac{1}{2}$ inches, and found the results sensibly the same. The origin of the error in my former observations I have been unable to detect; but it is probably to be ascribed to some fault in the connections of the cells.

The advantages of the concentric cylindrical arrangement of the elements of a voltaic circuit are very considerable; both in the scientific analysis of its complex actions and in its practical applications. The absolute restriction of the influence of the metallic plates to one side respectively, and the known definite relations of their surfaces and diameters, render the necessary calculations for the former obvious and easy; while for the latter, the reduction of the size of the generating metal, and the large quantity of the electrolyte which it admits of, give facilities for the maintenance of an energetic and constant current of force which no other arrangement can supply with equal effect.

I have already observed† that the position of the rod within the cylinder is immaterial to the effects, and it is obvious, that wherever placed, their mean distances, and consequently the mean section of the interposed electrolyte, must be the same.

A zinc rod of half an inch in diameter, placed in the axis of a copper cylinder $3\frac{1}{4}$ inches diameter, produces a certain effect, which is scarcely augmented in an appreciable degree by a second, or even a third similar rod placed in contact with it: the results of experiment were as follows:—

1 rod = 2·2
2 rods = 2·4
3 rods = 2·5

* Philosophical Transactions, 1839, p. 90.

† Ibid. 1838, pp. 44, 49.

Each rod separately would have been capable, in its position, of producing the full effect of one; but each was screened by the two others from the full aspect of the conducting cylinder, and but a slight advantage was gained from the combination by a slight increase of the section of the electrolyte, uncompensated by any increase of distance.

I anticipated that, if each rod were removed as nearly as possible to the sides of the cylinder, so as to be equidistant from the other two, the screening influence could not take place to the same extent, and that a greatly-increased effect would be produced. A glance at the annexed diagram will explain the difference of the two arrangements; fig. 1. representing a section of the first, and fig. 2. of the second.

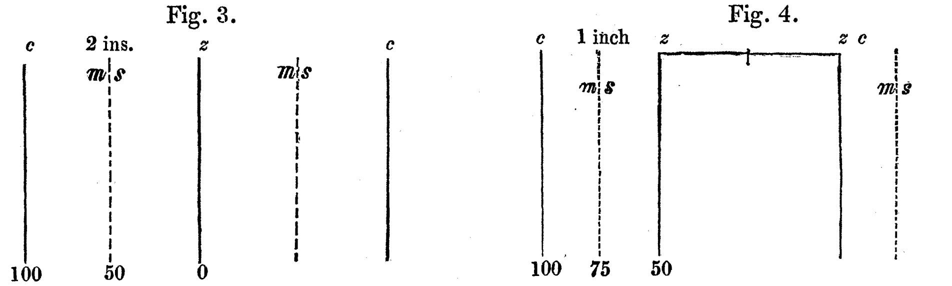
Fig. 1. Fig. 2.

Upon making the experiment, as in fig. 2, with the rods and cylinder of the last experiment, the result was increased to 3·1.

I also tested the conclusion with the large battery of ten cells of four inches diameter, and obtained from single rods $10\frac{1}{2}$ cubic inches of mixed gases per minute, and from two rods placed as near to the sides of the cylinders as possible, fourteen cubic inches per minute.

The law of the exact compensation of the greater resistance arising from the increased thickness of the electrolyte, by the extension of the area of its mean section, is of course only mathematically correct where the interior wire is infinitely small, but practically the half-inch rods bear so small a proportion to the cylinders which I have been in the habit of employing, that the results are not materially affected by their dimensions. When, however, the interior cylinders are enlarged, the thickness of the electrolyte is decreased, and the area of its section increased at the same time, and the circulating force rapidly augments. The results are easily submitted to calculation.

Fig. 3. Fig. 4.



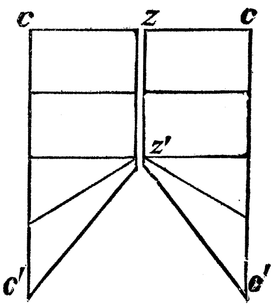
Let *c c*, fig. 3, represent a section of a copper cylinder four inches in diameter, and

z an infinitely small zinc rod in the axis. Let the area of the copper-plate be 100, the area of the mean section of the electrolyte ($m\ s$) will be $= 50$. The distance of c from z, or the thickness of the electrolyte, will be 2 inches. Let the rod z be replaced by a cylinder of zinc $z\ z$, two inches in diameter, fig. 4. The mean section will be increased to 75, and the thickness of the electrolyte will be decreased to 1 inch.

The force would, therefore, be increased in the proportion of 50 : 75 for the first, and of 1 : 2 for the second: consequently, compounding the proportions, the force circulating in the first arrangement would be to that in the second as 1 : 3.

In the preceding observations the cylinders and rods have been taken of equal heights; when one is shorter than the other, it will be obvious, from a little consideration, that the decrease of length is equivalent to an increase of distance between the two.

Fig. 5.



Let $c\ c\ c'\ c'$ represent a section of a copper cylinder, and $z\ z'$ a zinc rod of half its height; in any action which may take place from the point of the rod z' to the lower half of the cylinder c', the distance between the metals $z'\ c'$, or virtual thickness of the electrolyte being greatly augmented, the influence of the lower half will be proportionally diminished.

In some experiments which were carefully made with the calorific galvanometer, an amalgamated zinc rod was successively immersed in the electrolyte in a copper cylinder $3\frac{1}{2}$ inches high to the following depths, and with the results set down in the Table:—

Length of Zinc.	Degrees of galvanometer.
$\frac{1}{4}$ inch	7
$\frac{1}{2}$ inch	19
$\frac{3}{4}$ inch	35
1 inch	49
$1\frac{1}{4}$ inch	67
$3\frac{1}{2}$ inches	97

In a copper cylinder, twenty-one inches in height, charged with dilute sulphuric acid and sulphate of copper, an amalgamated zinc rod lost 51·5 grains in five minutes; a rod of half the length lost in the same time 26·1 grains. In a similar cylinder, six inches in height, charged in a similar manner, a zinc rod of equal length lost 12 grains; a rod of half the length lost 6·6 grains in the same time. The results, therefore, of each cylinder may be taken as directly proportioned to the lengths of the rods immersed in them.

Let us now turn from the consideration of simple circuits, and examine the law of a series, or of compound circuits. OHM's formula for these is

$$\frac{n\mathrm{E}}{n\mathrm{R}+r}=\mathrm{A},$$

in which n represents the number of the series.

Now so long as the external resistance (r) interposed in the circuit is merely metallic, the expression accords strictly with the results of experiment; and by doubling the number of cells at the same time that we double the efficient surface in each cell, we obtain an effect exactly double: thus by the formula

$$2\left(\frac{n\mathrm{E}}{n\mathrm{R}+r}\right)=\frac{2n\mathrm{E}}{\frac{2n\mathrm{R}}{2}+r}=\frac{2n\mathrm{E}}{n\mathrm{R}+r};$$

since in doubling the surface in each cell, *cœteris paribus*, we halve the resistance.

When, however, a voltameter or other chemical resistance is interposed in a circuit, OHM's formula will not hold, unless the opposite electromotive force which arises from the decomposition of the electrolyte, and consequent accumulation of ions upon the electrodes of the decomposing cell, be taken into consideration. This is of the same nature as the contrary electromotive force in the cell which we have already pointed out and designated by e' in the formula $\mathrm{E}=(\mathrm{B}-b-e')$. Professor WHEATSTONE, from a series of experiments made conjointly with myself, with my battery, and published in my fifth letter to you, inferred that, if this contrary electromotive force be assumed to be constant and be represented by e and introduced into the formula, thus

$$\frac{\mathrm{E}-e}{\mathrm{R}-r}=\mathrm{A},$$

tables might be calculated which would represent, approximatively, the quantity of decomposition for any number of cells of a given battery, while the results obtained by regarding the voltameter merely as a resistance, are, it is evident, widely at variance with the truth. Professor WHEATSTONE devised the following simple means to determine, on this supposition, the values of this contrary electromotive force, and of the added resistance, including that of the voltameter, without having recourse to any other measuring instrument than the voltameter itself. To obtain the value of the contrary electromotive force, he compared two experiments in which the resistances remained the same, while the sum of the electromotive forces alone varied. It is obvious that, if there existed no contrary electromotive force, the measured effect in the two cases should be simply as the number of elements in the series employed. A battery of five single cells should have half the power of a battery of ten double cells; but instead of this the effects measured by the voltameter were as 6 : 20.

$$\frac{10\mathrm{E}-e}{\frac{10}{2}\mathrm{R}+r}:\frac{5\mathrm{E}-e}{5\mathrm{R}+r}::20:6,\ \text{whence } e=2{\cdot}857\,\mathrm{E}.\quad .\quad .\quad .\quad .\quad (\alpha.)$$

The value of r in the formula, i. e. the resistance which the voltameter and connecting wires add to the circuit, will be ascertained in the following manner. The comparison was made with two batteries, one single and the other double, of ten cells each; the sum of the electromotive forces, therefore, remained the same, while the resistances only varied:

$$\frac{10\,E - e}{10\,R + r} : \frac{10\,E - e}{\frac{10\,R}{2} + r} :: 12{\cdot}5 : 20, \text{ whence } r = 3{\cdot}333\,R. \quad . \quad . \quad . \quad (\beta.)$$

Substituting the values thus found in the general formula $\frac{n\,E - e}{n\,R + r}$, he obtained the following results:—

Number of cells	3	4	5	10	15	20	
Quantity of gas calculated .	$\frac{5}{8}$	$3\frac{3}{5}$	6	$12\frac{18}{25}$	$15\frac{21}{25}$	$17\frac{13}{25}$	cubic inches.
Quantity of gas observed . .	$1\frac{1}{8}$	$3\frac{7}{8}$	6	$12\frac{1}{2}$	$15\frac{3}{4}$	$17\frac{1}{2}$	cubic inches.

The existence of such a contrary electromotive force, and its great energy, are amply attested by connecting the platinum plates of a voltameter, which has been some time in action, with a galvanometer; but I purpose to show the *general agreement* of the amended formula with the results of various and most trying combinations of different batteries, many of which were obtained without the slightest suspicion of the conclusions which might be derived from them. I say *general agreement*, for the extremely complicated nature of the actions to be measured, subjected as they were to the necessarily variable influence of circumstances affecting them, the large scale upon which the experiments were carried on, and the roughness and imperfection of the modes of measurement, would necessarily preclude the expectation of absolute accuracy. The remainder of the experiments, already published in my fifth letter, made with circuits which contained an equal number in series, but in which they were combined as double, treble, quadruple cells, &c., do not furnish results according with theory so well as might have been expected; they were therefore repeated with great care, and combined in various ways. The details of these experiments will presently appear. The first series was made with a constant battery composed of copper cylinders, six inches high, $3\frac{1}{2}$ inches in diameter, charged in the usual way with dilute sulphuric acid and sulphate of copper.

The first thing to be done was to determine the value of e in these combinations in the modified formula, by comparing the results of two arrangements in which the sums of the electromotive forces might vary, while the resistance remained the same. Thus

Cubic inches.

in five single cells, $\frac{5\,E - e}{5\,R + r} = 11{\cdot}25$ by experiment;

in ten double cells, $\frac{10\,E - e}{\frac{10\,R}{2} + r} = 33{\cdot}7$ by experiment;

therefore $5\,E - e : 10\,E - e :: 11{\cdot}25 : 33{\cdot}7$, or $e = 2{\cdot}49\,E$.

To determine the value of r in the formula, we might compare, in a similar manner, as pointed out by Professor WHEATSTONE, the results of two arrangements, in which the electromotive forces being equal, the resistances in the cells alone should vary. As, however, from the complicated nature of the arrangements, and the variability of different influential circumstances to which I have before alluded, I found it impossible to obtain two perfectly unexceptionable results for the comparison, I thought it allowable to take the mean of several; and from this I found that, with a voltameter whose platinum plates are three inches in length by one inch in width, a quarter of an inch apart, and charged with the standard dilute sulphuric acid, (sp. gr. 1·126), $r = 0·541$ R in a constant battery of the dimensions just described.

Now if a single cell of such a battery be taken and the circuits closed by a short thick wire, and the zinc rod forming the generating plate of the arrangement be weighed at intervals of five minutes, it will be found to lose 11·26 grs. for every such interval. This is a measure of the effective force of the circuit; and its equivalent in mixed gases is 25 cubic inches. This will be taken as the unit of work in the Table that follows, i. e. $\left(\frac{E}{R} = 1\right)$, and the calculated results for the different combinations will, in the third and fourth columns, be represented in fractions of this unit.

It is evident, that the amount of zinc, dissolved in such a single circuit, furnishes a measure of the maximum work that any number of such cells, combined in a single series, would be capable of performing; for $\frac{E}{R} = A$, and $\frac{nE}{nR + r}$ can never be greater than $\frac{E}{R}$, however great the value of n may be, so long as r has a positive value. In other words, however great the number of cells in a series, it is impossible, so long as any external resistance is interposed, that the result should be greater than that of a single cell in which no exterior resistance is opposed; although when r is very small when compared with n R, the results may be virtually equal.

If unity be taken to represent the maximum work that *any* single circuit can produce, then E will be represented by 1, and R also by 1, and

$$\frac{E}{R} = 1.$$

It is evident that in an effective circuit R can never equal E, but for the convenience of calculation it may be assumed to be so; and as all the quantities in the numerator are compared with E, and all in the denominator with R, the relative proportions will be exact. Taking the formula

$$\frac{nE - e}{nR + r} = A.$$

If $E = 1$ and $R = 1$, then $e = 2·49$, $r = 0·541$. Substituting different numerical values for n, we obtain for

		Calculation. Cubic inches.	Experiment. Cubic inches.
4 single cells,	$\frac{4 - 2{\cdot}49}{4 + 0{\cdot}541} = \frac{1{\cdot}51}{4{\cdot}541} = 0{\cdot}3325$	$= 8{\cdot}31$	7·5
4 double cells,	$\frac{4 - 2{\cdot}49}{\frac{4}{2} + 0{\cdot}541} = \frac{1{\cdot}51}{2{\cdot}541} = 0{\cdot}5942$	$= 14{\cdot}85$	13·7
4 treble cells,	$\frac{4 - 2{\cdot}49}{\frac{4}{3} + 0{\cdot}541} = \frac{1{\cdot}51}{1{\cdot}871} = 0{\cdot}8071$	$= 20{\cdot}17$	21
4 quadruple cells,	$\frac{4 - 2{\cdot}49}{\frac{4}{4} + 0{\cdot}541} = \frac{1{\cdot}51}{1{\cdot}541} = 0{\cdot}9799$	$= 24{\cdot}5$	25·5
4 quintuple cells,	$\frac{4 - 2{\cdot}49}{\frac{4}{5} + 0{\cdot}541} = \frac{1{\cdot}51}{1{\cdot}341} = 1{\cdot}126$	$= 28{\cdot}15$	30
5 single cells,	$\frac{5 - 2{\cdot}49}{5 + 0{\cdot}541} = \frac{2{\cdot}51}{5{\cdot}541} = 0{\cdot}453$	$= 11{\cdot}33$	11·25
5 double cells,	$\frac{5 - 2{\cdot}49}{\frac{5}{2} + 0{\cdot}541} = \frac{2{\cdot}51}{3{\cdot}041} = 0{\cdot}8254$	$= 20{\cdot}63$	20·5
5 treble cells,	$\frac{5 - 2{\cdot}49}{\frac{5}{3} + 0{\cdot}541} = \frac{2{\cdot}51}{2{\cdot}208} = 1{\cdot}137$	$= 28{\cdot}42$	28·7
5 quadruple cells,	$\frac{5 - 2{\cdot}49}{\frac{5}{4} + 0{\cdot}541} = \frac{2{\cdot}57}{1{\cdot}791} = 1{\cdot}401$	$= 35{\cdot}04$	35·2
10 single cells,	$\frac{10 - 2{\cdot}49}{10 + 0{\cdot}541} = \frac{7{\cdot}51}{10{\cdot}541} = 0{\cdot}7124$	$= 17{\cdot}81$	15·7
10 double cells,	$\frac{10 - 2{\cdot}49}{\frac{10}{2} + 0{\cdot}541} = \frac{7{\cdot}51}{5{\cdot}541} = 1{\cdot}355$	$= 33{\cdot}88$	33·7
15 single cells,	$\frac{15 - 2{\cdot}49}{15 + 0{\cdot}541} = \frac{12{\cdot}51}{15{\cdot}541} = 0{\cdot}8117$	$= 20{\cdot}29$	18·7
20 single cells,	$\frac{20 - 2{\cdot}49}{20 + 0{\cdot}541} = \frac{17{\cdot}51}{20{\cdot}541} = 0{\cdot}8524$	$= 21{\cdot}31$	22.

The agreement of the calculated and experimental results under such complicated circumstances, as shown in the last two columns of the preceding Table, must, I think, be deemed very satisfactory; and it is worthy of remark, that the result just named, of the independent experiment with the single cell, 25 cubic inches, is almost identical with that deduced from the experimental determination of five cells; taking 11·25 cubic inches to represent accurately the fraction 0·453: and indeed agree very closely with the calculated results of the above Table, whatever combination be taken as the foundation of the calculation.

In the experiments already alluded to, which I performed in conjunction with Professor Wheatstone, the cells of the battery used were of the same character as the last, but with an efficient length of 20 inches, or 3·33 times greater. The duration of each experiment was in this case one minute.

Upon making the calculations for these, E being = 1, R = 1, e was found = 2·85, by comparing the results of five single with those of ten double cells; and r (by a mean of seven experiments) = 1·757. Hence we find,

		Calculation. Cubic inches.	Experiment. Cubic inches.
5 single cells,	$\frac{5-2·85}{5+1·757}=\frac{2·13}{6·757}=0·3182=$	7·31	6
5 double cells,	$\frac{5-2·85}{\frac{5}{2}+1·757}=\frac{2·13}{4·257}=0·505=$	11·59	11
5 treble cells,	$\frac{5-2·85}{\frac{5}{3}+1·757}=\frac{2·13}{3·423}=0·6281=$	14·4	14
5 quadruple cells,	$\frac{5-2·85}{\frac{5}{4}+1·757}=\frac{2·13}{3·007}=0·715=$	16·44	15·66
10 single cells,	$\frac{10-2·85}{10+1·757}=\frac{7·13}{11·757}=0·6081=$	13·98	12·25
10 double cells,	$\frac{10-2·85}{\frac{10}{2}+1·757}=\frac{7·13}{6·757}=1·058=$	24·33	20
20 single cells,	$\frac{20-2·85}{20+1·757}=\frac{17·13}{21·757}=0·7882=$	18·55	17·25.

These results again exhibit a general accordance with the calculation, but by no means so close as the preceding. I was therefore induced to repeat the experiments with great care. The following Table shows the results, which it will be seen closely correspond with those deduced by the formula.

By a mean of fourteen experiments r was again determined to be in this battery 1·725 R.

Taking, as before, E = 1, R = 1, and e = 2·49, we obtain from

		Calculation. Cubic inches.	Experiment. Cubic inches.
5 single cells,	$\frac{5-2·49}{5+1·725}=\frac{2·51}{6·725}=0·3732=$	8·58	8·875
5 double cells,	$\frac{5-2·49}{\frac{5}{2}+1·725}=\frac{2·51}{4·225}=0·5941=$	13·66	13·5

		Calculation. Cubic inches.	Experiment. Cubic inches.
5 treble cells,	$\frac{5-2{\cdot}49}{\frac{5}{3}+1{\cdot}725}=\frac{2{\cdot}51}{3{\cdot}391}=0{\cdot}738$	$=16{\cdot}97$	17·0
5 quadruple cells,	$\frac{5-2{\cdot}49}{\frac{5}{4}+1{\cdot}725}=\frac{2{\cdot}51}{2{\cdot}975}=0{\cdot}8437$	$=19{\cdot}4$	20·0
10 single cells,	$\frac{10-2{\cdot}49}{10+1{\cdot}725}=\frac{7{\cdot}51}{11{\cdot}725}=0{\cdot}6408$	$=14{\cdot}73$	15·25
10 double cells,	$\frac{10-2{\cdot}49}{\frac{10}{2}+1{\cdot}725}=\frac{7{\cdot}51}{6{\cdot}725}=1{\cdot}116$	$=25{\cdot}68$	25·5
20 single cells,	$\frac{20-2{\cdot}49}{20+1{\cdot}725}=\frac{17{\cdot}51}{21{\cdot}725}=0{\cdot}8062$	$=18{\cdot}54$	18·00.

The maximum work of a single circuit of this battery was found to be 9·95 grs. of zinc per minute, which is equivalent to twenty-three cubic inches of the mixed gases. A similar agreement of this independent result which has been taken as the unit in the preceding table $\left(\text{for } \frac{E}{R}=1\right)$ with those which would be afforded by any combination of cells taken as the foundation of the calculation may be also observed, as in the case of the table deduced from experiments with the smaller battery.

When a number of cells of different power are included in the same circuit, the expression becomes

$$\frac{n\,E+n'\,E'-e}{(n+n')\,R+r}=A,$$

supposing that R remains the same as in the regular circuit, and E′ represents the electromotive force of the new element, and n' the number of the new elements included.

It will further, on a little consideration, be obvious why a half-zinc rod may be substituted for a whole one in a series, without any perceptible diminution of the effect, as I found upon a former occasion*. The effect of diminishing the length of the rod is principally to increase the distances between the metals, as the dimensions of the mean section of the electrolyte will scarcely be altered, owing to the comparatively small surface of the generating metal, even when entire. The general formula will then become

$$\frac{n\,E-e}{n'\,R+n''\,R'+r}=A,$$

when n' represents the number of ordinary zinc rods, n'' the number of shortened ones, and R′ the increased resistance offered by each of the latter.

The mean distance between the metals will, perhaps, be increased one-third by

* Philosophical Transactions, 1836, p. 127.

halving the length of the zinc; and the resistance R presented by that cell, varying directly as the distance, will be $1\frac{1}{3}$ instead of one.

The formula, therefore, for 20 small cells with 19 zinc rods of the ordinary size, and 1 short one, becomes

$$\frac{20 - 2{\cdot}49}{19 + 1{\cdot}33 + 0{\cdot}541} = \frac{17{\cdot}51}{20{\cdot}871} = 20{\cdot}97 \text{ cubic inches}$$

instead of

$$\frac{20 - 2{\cdot}49}{20 + 0{\cdot}541} = \frac{17{\cdot}51}{20{\cdot}541} = 21{\cdot}31 \text{ cubic inches,}$$

when the zincs are all of the full length.

Thus with a small series of five cells with entire rods

$$\frac{5 - 2{\cdot}49}{5 + 0{\cdot}541} = \frac{2{\cdot}51}{5{\cdot}541} = 11{\cdot}33 \text{ cubic inches;}$$

with four entire rods and one half rod,

$$\frac{5 - 2{\cdot}49}{4 + 1{\cdot}33 + 0{\cdot}541} = \frac{2{\cdot}51}{5{\cdot}871} = 10{\cdot}69 \text{ cubic inches;}$$

the differences not being appreciable in the usual mode of measurement.

In an arrangement containing one or more reversed cells, the formula becomes

$$\frac{(n - n')\,\mathrm{E} - e}{(n + n')\mathrm{R} + r} = \mathrm{A},$$

where n' represents the number of reversed cells.

My fifth letter contains the results of experiments with the battery under such circumstances. Upon comparing these results with those of the formula just given, the discrepancies were found to be constant and considerable; such however as might be accounted for by supposing that each reversed cell introduced, in addition to the reversed current, an extra resistance. Upon searching for this resistance it was proved to exist, and its cause manifested by the following experiments.

Ten small cells, charged in the usual manner, were arranged in series, including a voltameter, and an additional cell with a similar charge; substituting a copper rod in the interior for one of zinc.

In four minutes seven cubic inches of gas were collected in the voltameter; the action then suddenly declined in intensity, and in the next four minutes only $3\frac{1}{2}$ cubic inches of gas were given off. Upon examining the copper rod it was found coated with a film of oxide: this was wiped off, and a bright metallic surface was again exposed, and on once more connecting the battery, seven cubic inches of gas were given off, as before, in four minutes. The quantity again declined. This was several times repeated, and always with the same general results. It is hence evident, that when copper is made the zincode in the series, a layer of oxide is deposited upon it, which is not immediately dissolved by the acid, and offers a resistance which will vary according to its thickness; and this again will much depend upon the size of the surface.

This is, moreover, not the only point for consideration; for it is probable that the hydrogen accumulated upon the zinc of the reversed cells would exalt its electromotive force, so that $-$ E would be somewhat increased; and upon making the calculation upon these amended data the formula becomes

$$\frac{n\,\mathrm{E} - n'\,\mathrm{E}' - e}{(n + n')\,\mathrm{R} + r + n'r'} = \mathrm{A}, \quad \text{or} \quad \frac{n\,\mathrm{E} - n'\,\mathrm{E}' - e}{n\,\mathrm{R} + n'\,\mathrm{R}' + r},$$

taking in the first formula r' to represent the additional resistance introduced by each reversed cell, and in the second R' as the total resistance in each reversed cell, and E' the increased electromotive force in each of the same reversed cells.

In the following calculation $\mathrm{E} = 1$, $\mathrm{R} = 1$, $e = 2{\cdot}85$, $r = 1{\cdot}725$, $\mathrm{E}' = 1{\cdot}1$, $r' = 0{\cdot}5$.

It is assumed that r' is a constant quantity, which may be pretty accurately true when the copper surface is so large in relation to the zinc as in the present case.

			Calculation. Cubic inches.	Experiment. Cubic inches.
20 direct,	$\frac{20 - 2{\cdot}85}{20 + 1{\cdot}725}$	$= \frac{17{\cdot}05}{21{\cdot}725}$	= 18·18	17·5
1 reversed,	$\frac{19 - 2{\cdot}85 - 1{\cdot}1}{20 + 1{\cdot}725 + 0{\cdot}5}$	$= \frac{15{\cdot}05}{22{\cdot}225}$	= 15·57	15·5
2 reversed,	$\frac{18 - 2{\cdot}85 - 2{\cdot}2}{20 + 1{\cdot}725 + 1{\cdot}0}$	$= \frac{12{\cdot}95}{22{\cdot}275}$	= 13·1	12·75
3 reversed,	$\frac{17 - 2{\cdot}85 - 3{\cdot}3}{20 + 1{\cdot}725 + 1{\cdot}5}$	$= \frac{10{\cdot}85}{23{\cdot}225}$	= 10·74	10·5
4 reversed,	$\frac{16 - 2{\cdot}85 - 4{\cdot}4}{20 + 1{\cdot}725 + 2{\cdot}0}$	$= \frac{8{\cdot}75}{23{\cdot}275}$	= 8·48	8·5
5 reversed,	$\frac{15 - 2{\cdot}85 - 5{\cdot}5}{20 + 1{\cdot}725 + 2{\cdot}5}$	$= \frac{6{\cdot}65}{24{\cdot}225}$	= 6·31	5·5
6 reversed,	$\frac{14 - 2{\cdot}85 - 6{\cdot}6}{20 + 1{\cdot}725 + 3{\cdot}0}$	$= \frac{4{\cdot}55}{24{\cdot}725}$	= 4·23	3·5
7 reversed,	$\frac{13 - 2{\cdot}85 - 7{\cdot}7}{20 + 1{\cdot}725 + 3{\cdot}5}$	$= \frac{2{\cdot}45}{25{\cdot}225}$	= 2·23	1·625
8 reversed,	$\frac{12 - 2{\cdot}85 - 8{\cdot}8}{20 + 1{\cdot}725 + 4{\cdot}0}$	$= \frac{0{\cdot}35}{25{\cdot}725}$	= 0·31	1·16

The agreement of the experiments with the calculations is not as close as before, especially in the lower part of the table, but may I think be deemed satisfactory, as a first approximation to the solution of a problem of a most complicated nature.

The influence of the dimensions of the plates of a voltameter upon the amount of decomposition may also be submitted to calculation in the same way. This influence will, of course, be most perceptible when a small number of elements presenting a large surface is employed; whereas, when a numerous series is made use of, the dimensions of the electrodes are of little consequence. Some experiments which I have made with a large voltameter, kindly lent to me for the purpose by Mr. Gassiot, will place this in a striking point of view. The voltameter consisted of five pairs of platinum plates, each four inches by $3\frac{3}{4}$ inches, at an average distance of half an inch apart. These were so arranged that any number of them might at pleasure be connected with a battery.

20 cells of the small battery were so arranged as to form a series of 5 quadruple cells, and then connected with one pair of plates of the voltameter. By a mean of two experiments they gave 26·2 cubic inches of gases for five minutes.

When all the plates of the voltameter were connected with the battery, the product of gases for five minutes was 32 cubic inches.

The same battery arranged to form a series of 20 single cells, furnished with one pair of plates 16 cubic inches, and with all the plates the result was the same.

Now by experiment, if $E = 1$, $e = 2{\cdot}49$, $R = 1$, $r =$ resistance with one pair.

$$\left\{\begin{array}{lll} (1.) & \text{20 with one pair} & = \dfrac{20 - 2{\cdot}49}{20 + r} = \dfrac{17{\cdot}51}{20 + r} = 16 \text{ cubic inches.} \\ (2.) & \text{20 with five pairs} & = \dfrac{20 - 2{\cdot}49}{20 + \frac{r}{5}} = \dfrac{17{\cdot}51}{20 + \frac{r}{5}} = 16 \text{ cubic inches.} \end{array}\right.$$

$$\left\{\begin{array}{lll} (3.) & \text{5 quadruple with one pair} & = \dfrac{5 - 2{\cdot}49}{\frac{5}{4} + r} = \dfrac{2{\cdot}51}{1{\cdot}25 + r} = 26{\cdot}2 \text{ cubic inches.} \\ (4.) & \text{5 quadruple with five pairs} & = \dfrac{5 - 2{\cdot}49}{\frac{5}{4} + \frac{r}{5}} = \dfrac{2{\cdot}51}{1{\cdot}25 + \frac{r}{5}} = 32 \text{ cubic inches.} \end{array}\right.$$

Since the electromotive forces in the two last expressions are the same, we can, by comparing them, ascertain the value of r. Thus

$$1{\cdot}25 + r : 1{\cdot}25 + \frac{r}{5} :: 32 : 26{\cdot}2$$

$$r = \frac{18{\cdot}125}{52{\cdot}4} = \frac{1}{3} \text{ nearly.}$$

Now substituting this value of r in the expressions (1.) and (2.), and adopting the experimental result of 16 cubic inches, we obtain for

Calculation.

(1.) the fraction $\frac{17{\cdot}51}{20{\cdot}33} = 16{\cdot}2$ cubic inches.

(2.) the fraction $\frac{17{\cdot}51}{20{\cdot}06} = 16{\cdot}0$ cubic inches.

The calculated results it will be seen almost coincide with each other, as do the experiments.

By the substitution of different values for R and r in the formula, it will be found that every different arrangement must have a distinct number in series, which it will be most advantageous to work with, and this number will vary in the same arrangement, with the nature of the electrolyte, and also with the size of the battery plates. It will appear from calculation, that the most advantageous combination is that in which the value of A $\left(\text{in the formula } \frac{n \mathrm{E} - e}{n \mathrm{R} + r} = \mathrm{A}\right)$ most nearly approaches to 0·5. It will therefore vary even in batteries of the same chemical construction; increasing as R diminishes in proportion to r: or in other words, when the plates are large, a more numerous series is required, than when small, to produce the most advantageous results. This is likewise the case when the exterior resistance is increased: in both cases R is virtually diminished in respect to r.

It is evident from the preceding observations, that all the comparisons hitherto made by different experimenters between the general relative powers of different batteries are faulty, inasmuch as they only hold good in the particular cases to which the experiments are limited; and one battery of a certain size may be preferable for one kind of decomposition, and yet may allow of considerable useless expenditure of power when a different electrolyte is subjected to its action. As, however, great stress has, by some, been laid on comparisons of this kind, it may not be amiss to give a few experimental results.

In the following arrangements the cylindrical form was employed. In each case the platinum cylinders were 4 inches high, and 1¾ inch in diameter. The zinc rods were half an inch thick, the exciting fluid was placed in a porous earthenware tube 1 inch in diameter. Three cells was the number employed in each experiment. The measures employed was the quantity of mixed gas produced from the voltameter during 5 minutes.

Exterior liquids.	Exciting liquids.	Gas in five minutes.
		cubic inches.
Acid sulphate of copper	Dilute sulphuric acid, specific gravity 1·126	3·0
Nitric acid, specific gravity 1·40	Dilute sulphuric acid, specific gravity 1·126	14·0
Bichromate of potash, specific gravity 1·050	Dilute sulphuric acid, specific gravity 1·126	3·1
Bichromate of potash, ⅛ sulphuric acid	Dilute sulphuric acid, specific gravity 1·126	5·5
Nitrate of copper, neutral saturated solution	Dilute sulphuric acid, specific gravity 1·126	3·5
Nitric acid, specific gravity 1·40	Dilute nitric acid, specific gravity 1·056	8·5

The eligibility of a liquid in the construction of a battery will, of course, be much influenced by its conducting power: and it would at first sight appear that this might be easily determined by placing the different liquids, in succession, in the same voltameter, or experimental cell, and transmitting through them a constant current of known power; measuring the retarding influence of each by another voltameter charged in the usual way with dilute sulphuric acid, and included in the same circuit. The following are the results of some experiments so performed. The current from ten cells of the small constant battery was employed:—

Liquid tested.	Gas from voltameter in five minutes.
	Cubic inches.
Nitric acid, specific gravity 1·4	11
Nitric acid + ⅛ sulphuric acid	11
Dilute sulphuric acid (standard)	9·2
Dilute sulphuric acid saturated with sulphate of copper	9·2
Saturated solution of sulphate of copper	7·9
Bichromate of potassa, specific gravity 1·050	5·6

Let us however consider these results with reference to the formula. The expression for the arrangement used becomes

$$\frac{n\,E - e - e'}{n\,R + r + r'},$$

in which e' signifies the contrary electromotive force, introduced by the accumulation of the ions on the plates of the voltameter containing the liquid tested, and r' the resistance offered by the same. It is clear that we cannot estimate r', which we are attempting, unless e' is known or remains constant: now e' is not constant, since with nitric acid it vanishes probably altogether, and varies with each of the other substances employed.

If chloride of platinum were not too expensive to allow of its being employed as the exterior part of the electrolyte in contact with a platinum, conducting plate, e', or the contrary electromotive force would be wholly annihilated, as nothing but platinum would be thrown down upon the platinum, and it would constitute the most perfect possible arrangement, but would not much, if anything, exceed the efficiency of nitric acid.

In the nitric acid battery the electromotive force is nearly double that of the sulphate of copper arrangement, and consequently one cell of that construction is capable of effecting the decomposition of dilute sulphuric acid. It is evident that a similar series of calculations might be made for this battery and others in which different electrolytes are employed; R varying as before with the size and distance of the plates.

I have, however, done enough for the accomplishment of my present purpose; but must not conclude without expressing my obligations to my friend Dr. Miller for his able assistance, both in the performance of the experiments and the calculations of the results which I have now the pleasure of communicating to you.

I remain, my dear Faraday,

Very faithfully yours,

J. F. Daniell.

King's College,
12th April, 1842.