

PHILOSOPHICAL TRANSACTIONS.

VIII. *On the Gas Voltaic Battery.—Experiments made with a view of ascertaining the rationale of its action and its application to Eudiometry.*

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IN the Philosophical Magazine for December 1842, I have published an account of a voltaic battery in which the active ingredients were gases, and by which the decomposition of water was effected by means of its composition.

The battery described in that paper consisted of a series of tubes containing strips of platinum foil covered with a pulverulent deposit of the same metal; the platinum passed through the upper parts of the tubes, which were closed with cement, the lower extremities were open; they were arranged in pairs in separate vessels of dilute sulphuric acid, and of each pair one tube was charged with oxygen, the other with hydrogen gas, in quantities such as would allow the platinum to touch the dilute acid; the platinum in the oxygen of one pair was metallically connected with the platinum in the hydrogen of the next, and a voltaic series of fifty pairs was thus formed. With this battery the following effects were produced:—

1st. A shock was given which could be felt by five persons joining hands.

2nd. The needle of a moderately sensitive galvanometer was whirled round and remained permanently deflected 60°.

3rd. A gold-leaf electroscope was notably affected.

4th. A brilliant spark visible in broad day-light was given between charcoal points.

5th. Iodide of potassium, hydrochloric acid, and water acidulated with sulphuric acid were severally decomposed; the gas from the decomposed water was collected and detonated. The gases were evolved in the direction which the chemical theory would indicate, the hydrogen travelling in one direction throughout the circuit, and the oxygen in the reverse.

When distilled was substituted for acidulated water in the battery cells, the effects were similar but more feeble.

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The effects, though clear and decisive in themselves, were further tested by counter experiments, such as reversing the current by reversing the gases, &c. ; but these I need not here detail, as the electrical effects of the gas battery, when charged with oxygen and hydrogen, have since the publication of that paper been repeatedly verified. I further stated, that when carbonic acid and nitrogen were substituted for oxygen and hydrogen, no voltaic effects were produced ; that oxygen and nitrogen produced no effects, but that hydrogen and nitrogen did produce a voltaic current, which I attributed to the combination, with the hydrogen, of the oxygen of atmospheric air in solution ; this opinion will be further tested in the following paper.

The voltaic current generated by this battery I attributed to chemical synthesis, of an equal but opposite kind, in the alternate tubes, at the points where the liquid, gas, and platinum met, and the object of covering the platinum with the pulverulent deposit*, was to increase the number of these points, the liquid being retained upon the surface of the platinum by capillary attraction.

The point which appeared to me at that time as most important, was the beautiful instance of the correlation of natural forces exhibited by the fifth effect, in which gases by combining and becoming a liquid, transfer a force which is capable of decomposing a similar liquid, and causing its constituents to become gases ; heat, chemical action and electricity being all blended and mutually dependent.

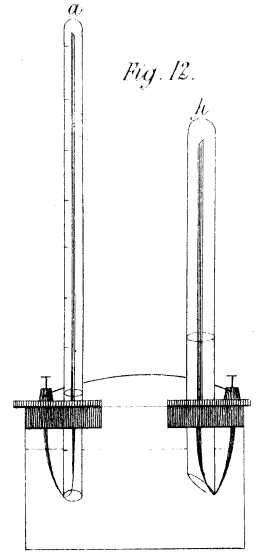
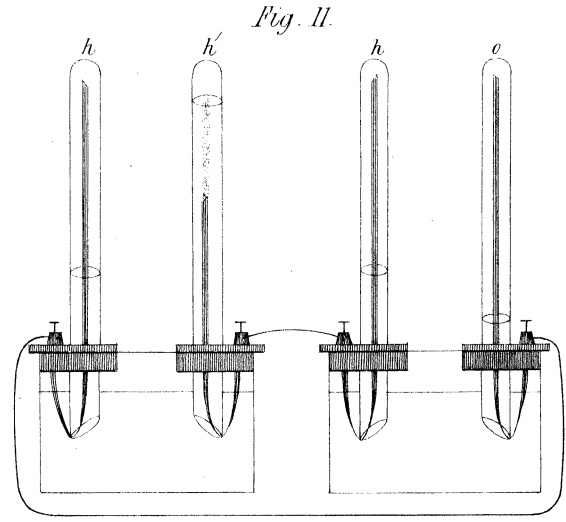
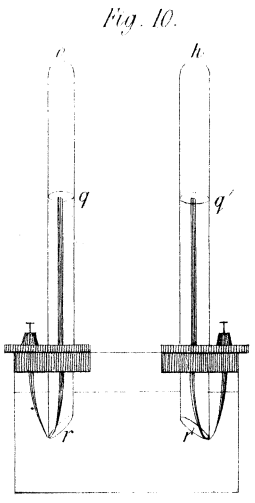
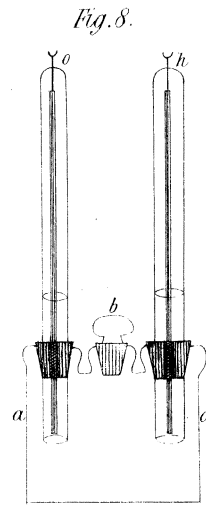
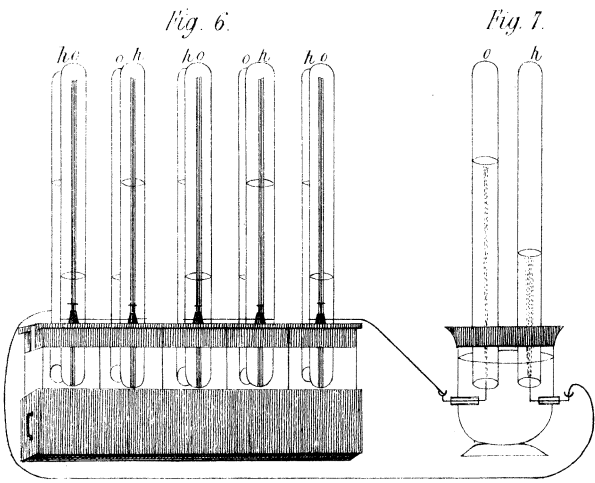
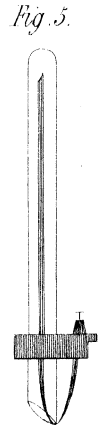
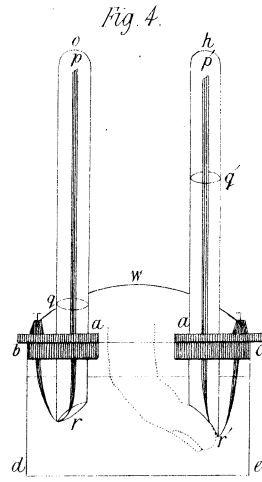
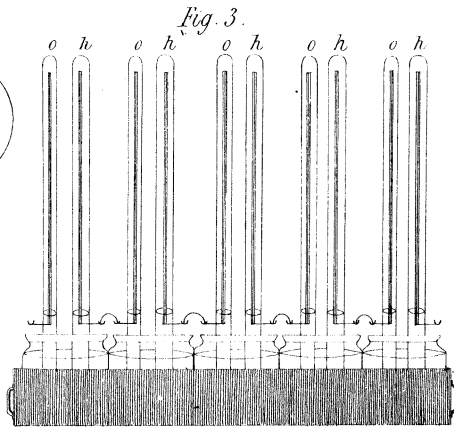
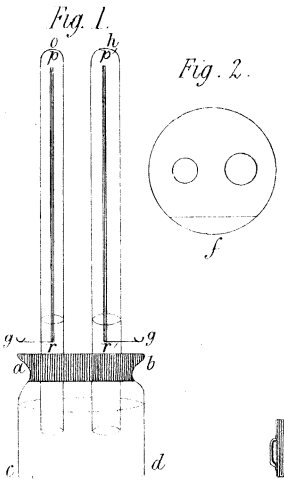
The apparatus with which I made the above experiments being composed of some pieces of tubing which happened to be in my laboratory, did not enable me to attain any precise accuracy of measure as to the volumes of gases absorbed, or to prove that FARADAY'S law of definite electrolysis finds no exception in the gas battery. Since that paper was written I have, after some failures, constructed apparatus by which I have been enabled to verify this law and to extend my researches into the nature of gaseous voltaic action. I have felt the more called on to multiply experiments on this subject, as a letter has been published on the gas battery, written by an electrochemist for whose opinion I have much respect, which attributes its action to a cause different from that to which I assigned it.

Soon after my original publication I received a letter from Dr. SCHÖNBEIN, the substance of which has since appeared in print†. Dr. SCHÖNBEIN there expresses an opinion, that in the gas battery oxygen does not immediately contribute to the production of the current, but that it is produced by the combination of hydrogen with water. I have recently heard a similar opinion to that of Dr. SCHÖNBEIN expressed by other philosophers, but I must take the liberty of dissenting from it and of adhering to that which I expressed in my original paper. My grounds of dissent will be seen in some of the ensuing pages.

In describing the apparatus used in the following experiments, I shall mention three forms of gas battery, with the first two of which my experiments were all performed ;

* For the method of effecting this see Mr. SMEE'S paper, Philosophical Magazine, April 1840.

† Philosophical Magazine, March 1843, p. 105.



the latter has only occurred to me while writing this paper. I have, therefore, not yet had an opportunity of trying it*, but it appears to me by far the best of the three, though, doubtless, superior modifications will shortly be discovered. Plate V. fig. 1 represents one of these forms; *a, b, c, d* is a wide-mouthed glass jar, into which a wooden plug, *a, b*, fits tightly by means of attached pieces of cork; this wooden cover is perforated to receive the tubes *o, h*, of which the size is such that the content of *h* shall be double that of *o*, and which are firmly cemented into it; the wooden cover is shown in plan in fig. 2; the piece *f* is capable of being detached at pleasure, in order to introduce a tube for charging the apparatus with gas; *p r, p' r'* are strips of well-platinized platinum foil, slightly curved like a cheese scoop to keep them erect and in the centre of the tube, and rivetted or welded to stout platinum wires, which are hermetically sealed into the glass, and terminate in brass mercury cups at *g, g*. This form of battery is charged by inverting it so as to fill the tubes with liquid; on reinversion the tubes may be charged with gas from a crooked tube and bladder. The apparatus (fig. 1.) is represented as charged and ready for use, and in fig. 3 is a battery of five cells, also represented as just charged.

The advantage of this form over that which I shall next describe, is the facility with which the tubes are filled with liquid, and the absence of any necessity of touching the electrolyte with the fingers. On the other hand, its disadvantages are the difficulty of examining the gases after experiment, and the impossibility of doing so during experiment without changing the electrolyte, as in order to examine the gases the whole apparatus must be immersed in a water-trough, and the cover with the attached tubes taken off while the jar and the ends of the tube are under water.

Fig. 4 represents a cell of the second form; *b, c, d, e* is a parallelepiped glass or stoneware vessel, such as is commonly used for the outer cells of the nitric acid batteries; the tubes are cemented into pieces of wood, *a b, a c*, and can with the wood be separately detached from the trough, as shown in fig. 5. At the aperture or space, *a a*, between the tubes there is just room for a finger to enter, close the orifice of either tube, and thus detach it from the apparatus. In this figure the platinum foil is turned up round the edge of the tube, instead of being attached to a wire sealed into the glass, and instead of a mercury cup there is a binding-screw connexion; but it is obvious that this part of the arrangement may be interchanged with the other apparatus, or varied *ad libitum*. This apparatus I have found in practice to be very much more convenient than the former, from the facility of detaching either tube so as to discharge some of the gas, if it be desirable to alter the level of the water-mark; or to examine or change the gas in any of the tubes. On the other hand, it has the disadvantage of requiring the finger to be immersed in the electrolyte, which, when the latter is of an active chemical character, is unpleasant and in some cases injurious. In fig. 6, a battery of five cells of this construction is represented as when charged with oxygen and hydrogen, and having been for some time connected

* See Postscript.

with a voltameter (fig. 7), the tubes of which are of the same size as those of the battery.

In the form last described (figs. 4 and 6), the tubes were all as nearly of the same size as could be procured; they contained each about $1\frac{1}{2}$ cubic inch; in the first form (figs. 1 and 3), the portion o, r of the narrow tube contained $1\frac{1}{4}$ cubic inch, and the portion h, r' of the wide tube contained $2\frac{1}{2}$ cubic inches. A portion of the apparatus with which I wrought was constructed by my order for the London Institution, and another portion belonged to Mr. GASSIOT, and was by him very kindly placed at my disposal for the purpose of these experiments; had it not been for this valuable addition, I should have been obliged to make all my experiments on a much smaller scale; they would have taken more time and been by no means so satisfactory.

As I have already stated, a third form has occurred to me while writing this paper, which I think in many respects more advantageous than either of the two preceding, and which, as it may be some time before I can experiment with it myself, I will here describe for the benefit of those who are differently situated. One cell of it is shown in fig. 8: a, a , is a Woulfe's bottle with three necks; in the centre neck is fitted a glass stopper, b ; in the other two the tubes o, h fit accurately by means of glass collars (c, c , fig. 9.) welded to them and ground on the outside; the platinum is hermetically sealed into the tops of the tubes, which may be charged in a similar manner to fig. 1. By immersing this apparatus in the water-trough, each tube with the gas it contains may be detached and examined separately, but its principal advantage is, that by slightly greasing the stopper and collars it may be made perfectly air-tight, which, for reasons that will be apparent in the course of this paper, is a most material point. This apparatus, moreover, being entirely composed of glass and platinum, concentrated acid, alkaline or other corrosive solutions, may be used as the electrolyte, without damaging the apparatus or introducing foreign matter.

In the experiments I am about to describe, the results were generally tested by chemical action, as manifested by the electrolysis, either of iodide of potassium or of water. I had at my disposal a highly sensitive astatic galvanometer, but I found such slight local actions disturb it, that a range of test experiments was in each case necessary to eliminate the true battery action from the accidental currents; and with all the pains that could be bestowed upon it, the results were less definite and trustworthy than those obtained with the iodide.

I may here state also, that, although with the battery described in my original paper when charged with oxygen, hydrogen and dilute sulphuric acid, I could not succeed in perceptibly decomposing water with less than twenty-six cells, yet the new arrangements, from their superiority in size and construction, were capable, when charged with the same gases and electrolyte, of decomposing water with four cells; and a single cell would decompose iodide of potassium.

Experiment 1.—Ten cells charged to a given mark on the tube with dilute sulphuric acid, sp. gr. 1.2, oxygen and hydrogen, were arranged in circuit with an interposed

voltameter*, as in figs. 6 and 7, and allowed to remain so for thirty-six hours. At the end of that time 2·1 cubic inches of mixed gas were evolved in the voltameter; the liquid had risen in each of the hydrogen tubes of the battery to the extent of 1·5 cubic inch, and in the oxygen tubes 0·7 cubic inch, equalling altogether 2·2 cubic inches; there was therefore 0·1 cubic inch more of hydrogen absorbed in the battery tubes than was evolved in the voltameter.

This experiment was several times repeated with the same general results; I give some of them in the annexed Table.

Cubic inch of oxygen absorbed in the battery cells.	Cubic inch of hydrogen absorbed in the battery cells.	Cubic inch of oxygen evolved in voltameter.	Cubic inch of hydrogen evolved in voltameter.	Time.	Number of cells.
0·7	1·4	0·7	1·4	36 hours.	10
0·5	1·2	0·5	1·1		
0·6	1·4	0·6	1·3		
0·6	1·3	0·5	1·2		
0·6	1·4	0·6	1·3		
Mean 0·6	1·34	0·58	1·26		

We may observe generally in these experiments, that the hydrogen evolved in the voltameter is somewhat more than double the volume of the oxygen, and that a still extra quantity of hydrogen is absorbed in the battery. With regard to the excess of hydrogen in the voltameter, this, as is well known to electricians, is always observable in the electrolysis of water, and has been attributed by FARADAY to the more ready solubility of oxygen, and its tendency to form oxygenated water †; but we have in the above experiments a still greater excess of hydrogen absorbed in the battery tubes; this result previous experiments had led me to expect. In one of these I found voltaic action produced by tubes charged alternately with hydrogen and water, and attributed it to the combination of hydrogen with the oxygen of atmospheric air in solution ‡. Granting for the moment this explanation to be correct, in a gas battery charged with oxygen and hydrogen we should have, upon completion of the circuit, three distinct voltaic actions:—First, the principal action occasioned by the gases in the tubes reacting upon each other through the medium of the electrolyte, *i. e.* reverting to fig. 4, an action in which the portions of the platinum exposed to the gases $p\ q, p'\ q'$, would be the efficient plates. Secondly, an action between the hydrogen at $p'\ q'$ and the air in solution in the neighbourhood of the immersed portion of the plate q, r ; this would add to the general current, but would tend disproportionately to diminish the hydrogen. Thirdly, a local action between the hydrogen at p', q' and the air in solution around the part q', r' ; this would add nothing to the general cur-

* These experiments were made with the battery fig. 1, though for more clearly showing the volumes of the gases the second form is represented in figures 6 and 7. The voltameter employed on this occasion had electrodes of fine platinum wire a quarter of an inch long. From the nature of the gas battery it is difficult to know the efficient surface of the plates. In ordinary batteries I have found, and stated some time ago, that for quantitative effects, the electrodes should be of the same size as the battery plates.

† Experimental Researches, § 716, 717.

‡ Phil. Mag., Dec. 1842, p. 419, Exp. 11.

rent, but would also tend to diminish the hydrogen. As this last is totally independent of the general action, it could be abstracted by merely placing a cell charged similarly to the battery out of the circuit with the terminals unconnected as in fig. 1; in a cell so placed the hydrogen was found to be absorbed in the ratio of rather less than 0.1 cubic inch in twenty-four hours.

On some occasions I found the rise of liquid in the hydrogen cell to be unequal in different tubes of the battery, and this I found more particularly the case in the battery fig. 4; it was some time before I discovered the cause of this. I will not enumerate my different conjectures, but state that which proved to be the correct one. As, in using the two forms of batteries (figs. 1 and 4), the chief difference consisted in the introduction of the finger, it occurred to me that my assistant's hands, which were employed in various manipulations, might, in placing the tubes in the cells of fig. 4, introduce into the electrolyte small portions of foreign matter, particularly metals, and that thus a local action might be occasioned; this view was strengthened by my frequently observing copper deposited upon some of the immersed portions of the platinum, and where this happened an excess of hydrogen was generally found to have been absorbed: to examine the accuracy of this view I caused

Experiment 2,—Four cells to be charged with a solution of sulphate of copper, and connected in closed circuit; after twenty-four hours' work, the liquid in the oxygen and hydrogen tubes had risen equally in three of the pairs, but in the fourth the liquid in the hydrogen tube had risen rather more than twice as high as in any of the others, and the whole of the platinum in this tube, from the water-mark downwards, was covered with metallic copper; it was thus evident that a slight precipitation having commenced on this platinum from some local circumstance which offered less resistance in this cell than in the others, a separate local current had been established, the hydrogen and the copper acting as a voltaic circuit, fresh copper had been constantly deoxidated at the expense of the hydrogen: the phenomenon is perfectly analogous to that observable in an ordinary sulphate of copper battery, when a slight portion of copper is deposited upon the zinc, and a local current is established by which the zinc is worn into a hole without contributing to the general current.

I have been thus particular in order to explain points in the action of this battery which might seem exceptions to the law of definite electrolysis, or what perhaps we should here call electro-synthesis; as a general result, the equivalent action of the battery was very beautiful; with fifty cells in action there was but a trifling difference in the rise of liquid in all the cells, and the rise of gas in the voltameter appeared so directly proportional, that an observer unacquainted with the rationale of a voltaic battery, would have said the gases from the exterior cells of the battery were conveyed through the solid wires and evolved in the voltameter; and had this been the first voltaic battery ever invented, this probably would have been the theory of its action.

In my original paper, I considered the points of voltaic action to be those where

the liquid, gas, and platinum met ; and it was to increase the number of these points that I employed platinized or spongy platinum ; indeed, from what I have since observed, I have much doubt whether I should have obtained any success had I used smooth platinum. The local action detailed in the last experiment, however, made me anxious to ascertain whether the principal points of action were those which I had originally believed, or whether the gases entered into solution first, and were then electro-synthetically combined by the immersed portion of the platinum ; whether, for instance, the efficient parts of the plates were the parts $p q$, $p' q'$ (fig. 4), or $q r$, $q' r'$. To ascertain this the following experiment was made :—

Experiment 3.—A battery of five cells was constructed, in which the platinum reached only to half the height of the tubes (see fig. 10). This was charged with oxygen and hydrogen, so that the liquid just covered the extremities of the platinum. In this case we have only the immersed portions of the platinum, $q r$, $q' r'$, and can examine the action of the gases which enter into solution, and are unaffected by the platinum until in solution. This battery so charged gave a very trifling action indeed ; it would not decompose iodide of potassium, and but slightly affected a highly sensitive galvanometer ; but when a little gas was added, so as to expose the platinum to the gaseous atmosphere, a considerable current was developed, and a single pair decomposed the iodide.

If, again, a battery of this description (fig. 10) be charged so that the water-mark is below the upper edge of the platinum, and the ends are connected in closed circuit, the liquid rises in both tubes until that in the hydrogen tube has reached the top of the platinum, and then there is no further rise. This experiment decides the question as to what is to be considered the working portion of the battery, but it does not positively decide whether solution and electrolysis are contemporaneous or successive, as it may be said that even what I have termed the exposed parts of the platinum are covered with a film of liquid. I should myself hesitate for the present to express a decided opinion on this point ; my first impression was, that there would be, as it were, three sets of points in contact, but I have not been able to devise an experiment definitively to settle this point*.

I aimed next at further establishing the analogies of this battery with the ordinary voltaic battery, *i. e.* regarding the hydrogen tube as analogous to the plate of zinc or other oxidable metal at the anode ; I wished to see how far this relation was borne out. It was beautifully shown in

Experiment 4.—Where a single pair was charged with oxygen and hydrogen, and a second with hydrogen in one tube, the other being filled with dilute sulphuric acid ; when the hydrogen of the second was metallically connected with the oxygen of the first, and the liquid of the second with the hydrogen of the first, as in fig. 11, bubbles of gas rose from the platinum, which proved, as I anticipated, to be hydrogen. In

* I have sometimes remarked when mixed oxygen and hydrogen have been collected in one tube of the gas battery over distilled water, the addition of a little sulphuric acid causes the gases rapidly to disappear.

short, though it required four pairs to decompose water with immersed platinum electrodes, yet the platinum in the atmosphere of hydrogen being analogous to an oxidable anode, one pair was with this assistance sufficient to decompose water, just as one pair of an ordinary battery will decompose water with an anode of copper.

The nitric acid battery, an account of which I originally published in 1839, having shown me the value of highly oxygenated acids and peroxides as voltaic excitants*, I determined, with a view of further extending the analogy of the gaseous and metallic voltaic batteries, to try the nitric acid as an electrolyte with the gas battery. Therefore,

Experiment 5,—I charged a battery with hydrogen and nitric acid in alternate cells, the nitric acid being only diluted sufficiently to prevent injury to the wooden parts of the battery. With this arrangement I found that three cells were capable of decomposing water, and thus, here also, the analogy held good, the gaseous hydrogen deoxidating the nitric acid in this arrangement, just as nascent hydrogen does in the metallic battery.

I now endeavoured to produce the converse effects, viz. to form a battery in which oxygen should be the gaseous element, and be absorbed by an electrolyte having an affinity for it. To this end,

Experiment 6,—I caused a battery of ten cells to be charged, the one set of tubes with oxygen and the alternate tubes with solution of protosulphate of iron. This battery decomposed iodide of potassium, but was not able to decompose water; the tubes which contained the solution of protosulphate represented the hydrogen tubes of the ordinary gas battery. The voltaic action caused by oxygen and protoxide of iron was, however, but temporary†. After a few hours it abated, the iodide was no longer decomposed, and the liquid did not rise perceptibly in the tubes containing oxygen; the solution when tested by ferrocyanide of potassium gave a blue precipitate, indicating the presence of peroxide, but the greater portion of this was probably formed at the expense of the atmospheric air.

In the last experiments and others, I had observed that a more decided effect was obtained when free hydrogen alone was present than when oxygen was alone. In my former paper I attributed this to the atmospheric air in solution, and for convenience of arrangement I have hypothetically assumed this explanation in the commencement of this paper, but the recent letter of Dr. SCHÖNBEIN induced me to look further into this point. Therefore,

Experiment 7,—I charged two batteries of two cells each, with hydrogen and dilute sulphuric acid in the alternate cells. When tested by iodide of potassium, each battery gave notable effects. One of these batteries was then placed, together with a cup containing phosphorus, in a shallow vessel of water; the phosphorus was ignited and a large glass vessel inverted over the whole; the terminal wires of the

* See Philosophical Magazine, May and October 1839, pp. 389 and 290.

† In experiment 26 it will be seen that a *continuous* current is obtained from oxygen and a liquid (ammonia); oxygen likewise gives a current with solution of cyanogen, and probably with many organic compounds.

battery, carefully protected by thick coatings of cement, passed under the edge of this vessel through the water, the exterior surface of which was covered with oil, more effectually to prevent the absorption of air. The terminal wires were then united and left so. After two hours, when the oxygen of the surrounding atmosphere had been exhausted by the phosphorus, the effect became more feeble, but continued throughout the evening. The next morning, however, the inclosed battery produced not the slightest effect upon the iodide, the liquid had risen in the hydrogen tubes about 0.2 cubic inch, but no other effect was perceptible. On the other hand, in the battery which had been placed by its side, charged in the same way, and similar in every respect but in the fact of being exposed to the atmospheric air, a very decided effect was produced; hydrogen had been evolved from one of the platins to the extent of 0.3 cubic inch in the cell containing liquid, and a decided effect was produced on the iodide. The two batteries were left in this state for three more days; the decomposition and the evolution of hydrogen continued in the exposed battery, but none was perceptible in the inclosed one, although the liquid had risen a little more, viz. 0.1 cubic inch in the hydrogen tubes of the latter. After the four days above mentioned, the jar of nitrogen which covered the battery was taken away, and the action of the battery was tested by iodide of potassium. At first there was no action, but after about fifteen minutes, a slight action was perceptible; this gradually increased, and in two hours the action was equal to that of the battery which had been from the first exposed to the atmosphere. I cannot but regard this experiment as a conclusive negation of that view which regards hydrogen and water as the efficient agents in the gas battery. The opinion appears to me to have arisen from the circumstance of our working always in an atmosphere containing oxygen, and also from the fact of this latter gas being more soluble than hydrogen*. If we lived in an atmosphere of hydrogen, and if this gas were equally or more soluble than oxygen, I have little doubt that the converse effects would be observed. A battery charged with hydrogen in one set of tubes and acidulated water in the alternate ones, at first gives an effect nearly equal to an oxygen gas battery, but the action rapidly declines in the former, while it is constant in the latter. Even the ordinary action of the gas battery when charged with oxygen and hydrogen appears to me unanswerable as to the point I am now discussing. When we see a battery of a number of cells at work, and the liquid gradually rising in the oxygen tubes, just in the proportion in which oxygen gas is eliminated in the voltameter, and when in a similar battery placed by its side, similarly charged, but not connected in closed circuit, not the slightest rise takes place in any tube, it seems impossible to adopt the conclusion that the oxygen has nothing to do with the current. Here we have no slight galvanoscopic effects, but chemical effects capable of quantitative admeasurement, capable of being continued to an extent only limited by the size of the apparatus, and equivalent to the chemical effects observable at the

* The tendency of oxygen to combine with platinum may also have its influence. See M. DE LA RIVE'S various experiments on this subject, *Bibl. Univ. passim*.

voltameter. If, on the other hand, hydrogen and water be the only active elements, what becomes of the hydrogen? If it combine with the water, we undoubtedly should by this means be able to obtain a suboxide of hydrogen*, a result of which I have not seen the slightest symptom in a long course of experiments on this subject. Even if we assume the action of the oxygen to be a depolarizing one, as suggested by Dr. SCHÆNBEIN, this comes to the same thing, as this depolarization can only be accounted for as being effected by the combination of the oxygen with hydrogen; and we might conversely assume this combination to be the efficient cause of the current, and the depolarization to take place in the hydrogen tubes. It seems to me that the effects at both anode and cathode are reciprocally dependent. The matter appears to me so clear that I should not have entered into detail upon it, were it not for the published letter of Dr. SCHÆNBEIN above mentioned, and that the superiority of the hydrogen is *primâ facie* very striking; knowing also the fondness with which we all adhere to preconceived opinions, as the consideration of the action of spongy or clean platinum on *mixed* gases led me to the discovery of the gas battery, I felt that I might be too apt to measure the correctness of my opinions by the success of the experiments to which they led, and therefore hesitated too confidently to rest upon what appeared to my mind positive demonstration.

Having verified the rationale of the action of the gas battery, I now sought to extend it to other gases, and caused arrangements of ten cells to be charged with such gases as were sufficiently insoluble to remain in the tubes time enough for experimental investigation. In all the following experiments, besides the ten cells charged in series, a single cell charged with similar gases and electrolyte was placed by the side, but with the terminals unconnected: thus, when the battery circuit had been closed for some time, by comparing the changes which had taken place in the battery tubes with those in the detached and unconnected pair, the effects due to solution, local currents, or other causes could be abstracted from those due to circulating voltaic action.

I shall arrange the following experiments in the order in which I instituted them, making such comments as may be necessary to explain my own deductions from the resulting phenomena. When not otherwise mentioned, the electrolyte will be considered as dilute sulphuric acid, sp. gr. 1.2.

Experiment 8.—A battery charged with oxygen and protoxide of nitrogen produced no effect upon iodide of potassium. Examined next day the liquid had not risen in the oxygen tubes; in the protoxide tubes it had risen to an average of 0.3 cubic inch, both in the battery and detached pair.

Experiment 9.—Oxygen and deutoxide of nitrogen produced a slight effect upon the iodide; the effect subsided after the circuit had been complete for a few minutes. On examining the battery after the circuit had been closed for twenty-four hours,

* I see by a recent paper of Dr. SCHÆNBEIN that he believes this to be the case, Archives de l'Électricité, No. 7, p. 73.

the liquid in the oxygen tubes had not risen; in the tubes containing deutoxide of nitrogen, the liquid had risen somewhat unequally in the different tubes to an amount averaging 0.2 cubic inch; in the detached pair it had risen to the same amount; not the slightest voltaic effect was now produced by the terminal wires.

Experiment 10.—Oxygen and olefiant gas decomposed the iodide, but rather feebly; after the circuit had been closed for twenty-four hours there was still a decomposition, which continued, but the action was extremely feeble. Two cells were allowed to remain arranged in closed circuit for fifteen days, a third being placed by the side, but with the terminals unconnected; at the expiration of this time the rise of liquid in the tubes was as follows:—

Rise of liquid in cells of closed circuit, in tubes of	Rise of liquid in cells of detached pair, in tubes of
Oxygen 0.05 cubic inch.	Oxygen 0.02 cubic inch.
Olefiant gas 0.4 cubic inch.	Olefiant gas 0.3 cubic inch.
Rise of liquid apparently due to voltaic action,	
In oxygen tubes	0.03 cubic inch.
In olefiant gas tubes	0.1 cubic inch.

These quantities are too small to enable any satisfactory inference to be deduced as to the equivalents of these gases which contributed to electrolysis; the more so as the rise of liquid was not quite uniform, and the action due to solution was so much greater than that due to electrolysis.

I do not feel entitled to draw any other conclusion from this experiment than that there was a very feeble voltaic current produced by these gases; both the remaining oxygen and the olefiant gas were unaltered in character.

Experiment 11.—Oxygen and carbonic oxide produced notable effects upon the iodide, and slight symptoms of decomposing water; a few bubbles gathered upon the electrodes of an interposed voltameter; the effects continued; and at the expiration of fifteen days, the following was the state of the tubes in two cells, put aside as in the last experiment:—

Rise of liquid in cells of closed circuit, In oxygen tubes	Rise of liquid in tubes of detached pair, In oxygen tubes
In carbonic oxide tubes 0.93 cubic inch.	In carbonic oxide tubes 0.7 cubic inch.
Rise of liquid apparently due to voltaic action,	
In oxygen tubes	0.1 cubic inch.
In carbonic oxide tubes	0.23 cubic inch.

Before the battery was charged for this experiment, the carbonic oxide had been carefully freed from carbonic acid by caustic potash. After action, the liquid gave a slight precipitate with lime-water, showing that carbonic acid had been produced by

the action. In this experiment the rise was more uniform in the different tubes than in the last, and the action more decided. The results, although on a small scale, appear more definite; thus we get the proportion as 1 : 2·3; and as the combining volumes of oxygen and carbonic oxide are as one to two, if we add the local action due to the oxygen of the air in solution, 1 to 2·3 is as near an approximation as can be expected. Though much superior to olefiant gas, the action of carbonic oxide is, however, very feeble when compared with that of hydrogen.

Experiment 13.—Oxygen and chlorine. Very considerable action on the iodide at first, but not constant; it abated within the first hour, and after twenty-four hours the action was extremely feeble, scarcely perceptible; the water had risen nearly to the top of the chlorine tubes, but the level in the oxygen tubes was unaltered. The chlorine was negative to oxygen, or in other words, the oxygen was in its voltaic bearing to chlorine as hydrogen to oxygen.

As in this experiment the water level in the oxygen tubes was unaltered, it appeared that this gas had little to do with the action, I therefore,

Experiment 14.—Charged the alternate tubes of a battery with chlorine and dilute sulphuric acid; the amount of action was much the same as in experiment 13, and equally transitory; a few gaseous bubbles were perceptible on the platinum in the oxygen cells, but not in sufficient quantity for examination. It is well known that chlorine of itself will slightly decompose water, forming hydrochloric acid, and evolving oxygen, and there is little doubt that the voltaic action here observed was due to this. There was no appearance of the platinum having been attacked in several experiments which I made with chlorine. So slight a chemical action will, however, give rise to voltaic effects, that the absence of any apparent corrosion is not conclusive. It is stated by chemists that gaseous chlorine will not attack platinum, but that it is only when nascent it combines with this metal; *non constat* however, that in the gas battery the chlorine at the initiatory instant of its electro-synthesis may not be in a state analogous, as to its chemical energies, to that converse state called nascent, and therefore we cannot venture to negative the possibility of the platinum being slightly attacked. This circumstance, added to its extreme solubility and power of decomposing water, makes chlorine rather an unsatisfactory element for the class of actions developed by the gas battery.

Solutions of bromine, chlorine and iodine, have been before experimented on (I believe by Dr. SCHENBEIN and M. BECQUEREL) as to their voltaic relations, but in examining the voltaic relations of bodies in a gaseous state, or to express myself with more caution, in a state passing from gaseous to liquid, I tried,

Experiment 15.—One set of tubes charged with gaseous chlorine, and the alternate tubes with solutions of bromine and iodine. The chlorine was negative to both, *i. e.* was to these as oxygen to hydrogen.

I now tried hydrogen with several gases, but as it was next to impossible (I found

it quite impossible), in experiments on a large scale, perfectly to exclude atmospheric air from the solution*, voltaic action was produced in every case; and as with one exception (chlorine) oxygen was the most powerful electro-negative gas, the action of the atmospheric air entirely masked any effect which might have been produced by the other gases†. I shall, therefore, not go through these experiments in detail, but mention one or two only which appear interesting, for the reasons which I shall state.

Experiment 16.—Chlorine and hydrogen gave very powerful effects, as was expected by Dr. SCHÖENBEIN‡; water was decomposed between platinum electrodes by two cells. This is the most powerful gas battery §, but not very satisfactory, for the reasons above stated, experiment 13.

Experiment 17.—Hydrogen and carbonic oxide were tried in order to ascertain their voltaic relations. Hydrogen was much more electro-positive than carbonic oxide, or rather formed, with the oxygen of the atmospheric air in solution, a combination which overpowered the opposite tendency of the carbonic oxide and air.

Experiment 18.—Chlorine and olefiant gas gave a very feeble effect upon iodide of potassium. After four hours the liquid in the olefiant gas tubes had not risen more in the closed circuit than in the detached pair; the chlorine was nearly all absorbed in solution.

Experiment 19.—Chlorine and carbonic oxide gave very notable effects; ten cells decomposed water. From the extreme solubility of the former gas, the equivalent relationship could not be ascertained.

It now occurred to me that as oxygen and hydrogen are evolved from water by electrolysis, and conversely form water by electro-synthesis, so some other gases which are evolved from certain electrolytes by voltaic action, might, when arranged as a gas battery with the electrolyte from which they are evolved, give rise to a current, although they would not do so when arranged in circuit with a different electrolyte. To test this view I tried,

Experiment 20.—Oxygen and deutoxide of nitrogen in alternate tubes of the gas battery, with dilute nitric acid; the effects were however precisely similar to experi-

* Gases will creep by a species of endosmose through water. Some time ago I kept inverted over water for two months, a vessel divided by a diaphragm of porous ware, on one side of which was oxygen gas, on the other hydrogen; the diaphragm was constantly wet from capillary attraction; at the end of that period the water had risen considerably, and the gases on each side detonated.

† See Postscript.

‡ See his letter, Philosophical Magazine, March 1843.

§ Chlorine, in its voltaic relations, may be considered as the converse of zinc, both decomposing water, but the one liberating oxygen, the other hydrogen; thus a tube of the gas battery charged with chlorine, and having acidulated water as an electrolyte, and zinc as a positive element, forms a combination of which one pair will decompose water. I have tried to render this combination practically useful, by charging the negative cell of a nitric acid battery with peroxide of manganese and muriatic acid, but the supply of chlorine thus obtained is insufficient for quantitative voltaic effects, though the intensity is great.

ment 8, viz. a very feeble action for a few minutes, then a cessation, and no continuous chemical action.

Experiment 21.—For the same reason oxygen and nitrogen, with solution of sulphate of ammonia, were tried; this arrangement produced at first a slight effect upon the iodide, which soon ceased, and after several days there was no more rise of liquid in any cell of the closed circuit than in the detached cell; the rise of liquid in both was very trifling indeed (about 0.01 cubic inch), and had evidently nothing to do with voltaic action. In this experiment, and in every experiment that I have tried, I have perceived a trifling action for the first few minutes. This I should have attributed to accidental causes, such as slight impurities in the gases, slight metallic deposits on the plates, &c., but that it is always in the direction which theory would indicate. Thus in the present experiment, the appearance of iodine indicated oxygen to have the same voltaic relation to nitrogen as it has to hydrogen. This temporary effect, therefore, appears to me analogous to that action called by continental experimentalists polarization, an apparent tendency to action, *i. e.* an arrangement of molecules preliminary to electrolysis, but incapable of producing a continued current. In this and many other experiments with the gas battery I have observed this effect, but have never been able to produce any chemical change or electro-synthetic absorption of nitrogen.

Experiment 22.—As oxalic acid when electrolysed evolves at the anode a mixture of oxygen and carbonic acid, and at the cathode hydrogen and carbonic oxide; for the reasons above stated, I charged a gas battery with carbonic acid and carbonic oxide in the alternate tubes, and with oxalic acid as an electrolyte; a slight effect was produced, the carbonic oxide being to the carbonic acid as hydrogen to oxygen; but the current was evidently due to the atmospheric air in solution combining with the carbonic oxide; this I proved by some of the test experiments before mentioned, which I need not recapitulate.

Experiment 23.—Hydrogen, nitrogen, and sulphate of ammonia. This combination also gave effects with which the nitrogen appeared to have nothing to do, this gas being perfectly unaffected; I tried other experiments on this point, but they all led to the same conclusion, viz. that my idea of realizing a voltaic action by conversion of the ordinary effects of electrolysis was erroneous. It may be that the above gaseous products of electrolysis are secondary, and that water is the only electrolyte in these cases; but for this, as for many other theoretical questions, there are so many arguments *pro* and *con*, that it is not worth while to dilate on them unless they can be shown to lead, or to be likely to lead, to some new valuable facts or natural relations.

Reviewing the above experiments, it appears that chlorine and oxygen, on the one hand, and hydrogen and carbonic oxide, on the other, are the only gases which were decidedly capable of electro-synthetically combining so as to produce a voltaic current*. I should perhaps except olefiant gas, which appears to give rise to a conti-

* See Postscript.

nuous though extremely feeble current; and the vapours of bromine and iodine, were they less soluble, would probably also be found efficient as electro-negative gases.

It now occurred to me that as several of these gases (take as an instance nitrogen) were absolutely without effect in the gas battery, this would form a valuable instrument for the analysis of atmospheric air or other mixed gases. I therefore procured,

Experiment 24.—Two narrow cubic inch tubes of seven inches long, carefully graduated into 100 parts. These were immersed in separate vessels of dilute sulphuric acid, and filled with atmospheric air exactly to the extreme graduation; the water-mark within the tube was examined when exactly at the same level as the exterior surface of the liquid; folds of paper were used to protect them from the warmth of the hands, and thus prevent expansion; the barometer and thermometer were examined, and every precaution taken for accurate admeasurement. One of these tubes was left empty in order to ascertain, and eliminate from the result, the effect of solubility. Into the other was placed a strip of platinized platinum foil, one quarter of an inch wide. This strip of foil was connected by a platinum wire with another strip placed in a tube of hydrogen and inserted in the same vessel. The apparatus is shown in fig. 12. After the circuit had been closed for two days, the liquid was found to have risen in the tube *a* twenty-two parts out of the 100; in the tube placed by its side, it had risen one division. The tubes were allowed to remain several days longer, but no further alteration took place. This analysis gives therefore twenty-one parts in 100 as the amount of oxygen in a given portion of air.

Experiment 25.—The tube *a* (fig. 12) was charged with nitrogen to a given mark, and 0.5 cubic inch of pure hydrogen added, the tube *b* was then charged with oxygen, and the circuit closed. Examined after twenty-four hours, the water had risen in the tube *a* exactly 0.5 cubic inch. The apparatus was left in this state for several days, but without any further effect; the voltaic action had thus perfectly exhausted the hydrogen and there stopped.

These experiments are sufficient to prove the accurate eudiometric action of the gas battery; performed on a large scale this method of eudiometry appears to me likely to possess some advantages. In the eudiometer of VOLTA, when gases containing oxygen are to be analysed, if the hydrogen added for detonation be impure, the result is of course erroneous. The same may be said of the detonation by spongy platinum, or by a wire heated by a voltaic current, which I formerly proposed*.

If, on the other hand, gases containing hydrogen are to be analysed, errors may result from any impurities in the oxygen which is added, or from inaccuracy in the measurement of either gas; in the electrolytic method of eudiometry, the quantity or purity of the hydrogen, in the one case, is of no importance, and in the other, the quantity or purity of the oxygen, that is, provided there be sufficient to exhaust the equivalent to be abstracted from the mixed gas subjected to eudiometry.

* Philosophical Magazine, Aug. 1841, p. 99.

It should be observed, that in these experiments only a single pair of the gas battery can be used, as, if more be employed, the electrolyte is likely to be decomposed, and gas added to the compound*. The process is rather slow, but I think very sure. Another valuable application of this process is, that it affords (in experiment 24) a simple method of obtaining nitrogen of unquestionable purity. I know of no method which effects this object so perfectly. All the oxygen of the air is abstracted, as well as that free oxygen which may be contained in the liquid; and by subsequently introducing a little lime-water into the tube *a*, the trifling quantity of carbonic acid may be removed, or the same thing may be at once effected by using caustic potash as the electrolyte in the apparatus fig. 12.

Probably many other applications of the gas battery may suggest themselves to other experimentalists, and obviously many more changes may be rung upon the gases employed, and curious and valuable results obtained; I have, however, in this paper given a sufficient number of experiments fairly to open the subject; each appears so suggestive of new ones that it is difficult to know where to stop.

The experiments on eudiometry, which I have last named, induced me to refer to Dr. HENRY'S paper on Gaseous Analysis†, and on reading it I was struck with a coincidence between the action of spongy platinum on mixed gases and the gas battery, a coincidence strongly confirmatory of the views which led me to its discovery. I will endeavour briefly to state these, and I state them, not as being absolutely correct, for differences of opinion may exist on this as on every other scientific matter, but as being those which existed in my mind prior to the experiments, and which are considerably, and to me unexpectedly, strengthened by the results embodied in the above-mentioned paper of Dr. HENRY.

My original deduction may be stated and exemplified as follows:—When pure or amalgamated zinc is immersed in acidulated water, the oxygen, as is well known, will not combine with the zinc; but touch both zinc and liquid with platinum and combination ensues, the platinum being unaltered. So with a mixture of oxygen and hydrogen, the gases, although in intimate contact, will not chemically unite, but touch them with clean platinum and more or less rapid combination ensues. Here also the platinum is unaltered. Leaving out of the case any purely hypothetical explanation, why may not effects so similar in their character be related in other respects? In the voltaic combination the platinum is heated during action, and if the surfaces, and consequently the quantity of electro-chemical action be considerable, it is ignited; so in the catalytic combination, if the platinum be thin and of large extent, or in the form of a sponge, which still more increases its surface, it is ignited. Why, therefore, may we not regard the detonation of gas by platinum as a voltaic effect? or the combination of oxygen and zinc by the presence of platinum a catalytic effect? The only difference is, that gases do not admit of that interchangeable relation of particles which we call electrolysis. The necessity for this interchange is,

* See Postscript.

† Philosophical Transactions, 1824.

however, removed when the gases are in a state of such intimate admixture that it is not requisite to convey the action through a chain of particles; in the gas battery this chain is supplied by the intervening electrolyte, and thus the same action which is local in the experiments of DÖBEREINER is circulating in the gas battery; the latter bears the same relation to the former as the action of the ordinary voltaic battery does to the normal phenomena of chemical affinity. This relation is confirmed by the facts detailed in the paper of Dr. HENRY, as the gases which he there found would combine by the presence of spongy platinum, are precisely those which will combine in the gas battery; thus oxygen and hydrogen combine rapidly, oxygen and carbonic oxide much more slowly, and oxygen and olefiant gas very feebly, so much so, as, in HENRY'S experiments, to require heat to induce combination. Of course chlorine and hydrogen, which will unite without platinum, will, *à fortiori*, unite with the aid of platinum, or they may in the gas battery occasion secondary action; the oxygen evolved by the decomposition of water by the chlorine combining with the free hydrogen in the tube. As oxygen and ammonia will, when at a slightly elevated temperature, combine by the influence of spongy platinum, forming water and leaving nitrogen, I now in order further to test this relation, tried

Experiment 26.—Ten cells of the gas battery were charged with oxygen and solution of ammonia, with a little sulphate of ammonia added to improve its conducting power. This arrangement produced a moderate effect upon the iodide, which was continuous; the liquid rose slowly but uniformly in the oxygen tubes; a gas was evolved in the alternate tubes, which proved to be pure nitrogen. After three weeks closed circuit, the gases collected, measured, and averaged gave for each tube,

Nitrogen evolved = 0·07 cubic inch.

Oxygen absorbed = 0·12 cubic inch.

Experiment 27.—To examine whether the alkaline character of ammonia had any thing to do with the effect, ten cells were charged with oxygen and solution of caustic potash, but produced no effect.

These experiments are strongly corroborative, and seem to me conclusive as to the relation between the action of the gas battery and catalysis by spongy platinum. Experiment 26 is also remarkable in regard to the binary theory of electrolysis, but upon this point I will not here enter.

Applying the hypothesis of GROTHUS to the gas battery, we may suppose that when the circuit is completed, at each point of contact of oxygen, water and platinum, in the oxygen tube, a molecule of hydrogen leaves its associated molecule of oxygen to unite with one of the free gas; the oxygen thus thrown off unites with the hydrogen of the adjoining molecule of water; and so on until the last molecule of oxygen unites with a molecule of the free hydrogen; or we may conversely assume that the action commences in the hydrogen tube. In all these cases we should ever bear in mind that we proceed by steps which nature, as hitherto tested by experiment, has not recognised. All we can safely predicate of the actions at anode and

cathode is that they are correlations ; although they take place at a distance, the one has no more been proved to take place without the other, or before the other, than height has been proved to exist without depth. I therefore allude to this hypothesis, not as literally adhering to it, but because it is generally received, and may tend to associate the action of the gas battery with the ordinary phenomena of electrolysis.

A number of hypotheses has been and may be proposed to account for these and other mysterious phenomenal relations ; they all agree in being assimilations of what is unfamiliar to what is familiar. They are undoubtedly useful as didactic illustrations, and it is as such that they have hitherto contributed to advance science. It is, however, a curious circumstance, and worthy of some consideration, that the voltaic hypothesis of GROTTIUS, the emissive and undulatory hypotheses of light and heat, and, as far as I am aware, all physical hypotheses hitherto propounded, represent natural agencies as effects of *motion* and *matter*. These two seem the most distinct, if not the only conceptions of the mind, with regard to natural phenomena, and when we try to comprehend or explain affections of matter which are not obviously modes of motion, we hypothetically or theoretically reduce them to it : the senses *perceive* the different effects of sound, light, heat, electricity, &c., but the mind appears capable of distinctly *conceiving* them only as modes of motion. Does not this supply an argument that all physical agencies are reducible to these elements of mental conception ? Or are we to look for new powers of mind, in other words, will greater familiarity with phenomena, at present recondite, enable the mind more clearly to comprehend them, and avoid the necessity of referring them theoretically to more familiar, and apparently more simple phenomena ? To pursue this curious inquiry would involve me in a discussion foreign to the object of this paper and to the general character of contributions to the Royal Society, but the question arises so immediately out of the subject, and is so necessary to explain my own view, that I trust this brief statement of it will be considered sufficiently pertinent. It touches upon that interesting, scarce definable boundary, where physical merges into metaphysical science.

There are one or two other theoretical points as to which the gas battery offers ground of interesting speculation ; the contact theory is one. If my notion of that theory be correct, I am at a loss to know how the action of this battery will be found consistent with it. If, indeed, the contact theory assume contact as the efficient cause of voltaic action, but admit that this can only be circulated by chemical action, I see little difference, save in the mere hypothetical expression, between the contact and chemical theories ; any conclusion which would flow from the one would likewise be deducible from the other ; there is no sequence of time in the phenomena, the contact or completion of the circuit and the electrolytical action are synchronous. If this be the view of contact theorists, the rival theories are mere disputes about terms. If, however, the contact theory connects with the term contact an idea of force which does or may produce a voltaic current independently of

chemical action, a force without consumption, I cannot but regard it as inconsistent with the whole tenor of voltaic facts and general experience.

Another point of theory suggested by the gas battery, is the relation of latent heat in the different cells of the battery and voltameter. According to our received theory of caloric, oxygen and hydrogen cannot assume the gaseous from the liquid state without rendering sensible heat latent. Now, as in the gas battery the gases evolved from the liquid in the voltameter must require and absorb precisely as much heat as is set free by the gases becoming liquid in each cell, it may be a curious subject of future inquiry (an inquiry which that beautiful instrument, the thermomultiplier, will materially aid) to ascertain whether the heat absorbed in the voltameter be exacted from surrounding bodies, or whether it be supplied by the action of the battery itself, i. e. as the chemical force in the voltameter is conversely equivalent to that in each cell of the battery, and the calorific force at the voltameter is also the converse equivalent of that in each battery cell, whether there is the same mutual dependence of the latter as of the former forces. The action in the voltameter of ordinary batteries would argue strongly against the proposition, that the heat is exacted from surrounding bodies, as it is well known that water when electrolysed has its temperature rather increased than diminished; and I have found, when decomposing water with the nitric acid battery at a rate of 150 cubic inches a minute, a very considerable augmentation of temperature in the liquid subjected to decomposition, so much so, that if the quantity was not considerable, it was heated to ebullition. Much of this adventitious heat may have arisen from the restriction of the circuit by the voltameter plates and connecting wires, but if the gas battery be supposed to supply exactly sufficient heat, or (to use a license of expression) to convert electricity into sufficient heat to satisfy the demands of the expanding gases,—each battery cell being able by the condensation of its respective gases to afford this supply,—a rise of temperature ought to be perceptible in the whole battery equal to the heat produced by the condensation of gases in all the cells, minus that of one cell. I have not as yet been able to detect any elevation of temperature due to the action of the gas battery, not having in my possession any instrument capable of detecting such delicate thermoscopic effects. I am, therefore, the more anxious to offer the point for the consideration of those who may have such instruments at their command; and here for the present I leave the gas battery and its theory.

*London Institution,
March 12th, 1843.*

POSTSCRIPT, July 7th.

The length of time which has elapsed between the communication and printing of this paper, as it has enabled me to procure the apparatus fig. 8, will I trust be deemed

a sufficient reason for my adding a Postscript containing a few experiments with this form of battery, some of which I cannot but consider important.

Experiment 28.—In order farther to test the opinion expressed, p. 105, six cells of this battery were charged with pure hydrogen and dilute acid in the alternate tubes. When first charged they decomposed water freely, but after the circuit had been closed for a short time, to exhaust the oxygen of the atmospheric air in solution, they produced no voltaic effect; the whole series of six would not decompose iodide of potassium; when, however, a little air was allowed to enter any one of the tubes containing liquid, that single cell instantly decomposed the iodide; three cells were put aside, each in closed circuit; at the expiration of a week these produced no effect upon a galvanometer, nor was there any gas evolved in the tubes containing liquid; the stoppers were now taken out, and the liquid in the hydrogen tubes rose to an average of 0.3 cubic inch; each cell contained a pint, and we may therefore regard 0.15 cubic inch as the amount of oxygen held in solution by this quantity of acidulated water. Were it not for the extreme practical difficulty of perfectly excluding atmospheric air for a long period, the above would furnish an excellent method of examining the quantity of oxygen held in solution by water, and by applying the proper calculus we might read off on our galvanometer scale the infinitesimal bubbles of gas contained in a given bulk of liquid; if, however, the acid water or the hydrogen contain foreign ingredients, a very different result follows, and the liquid, for reasons which will now be obvious, frequently rises considerably in the hydrogen tubes.

Experiment 29.—I repeated experiment 24 with the battery fig. 8, expecting that as the external air was shut out I should obtain the result more speedily; I was indeed not without a vague hope of producing some effect upon the nitrogen. The first result did follow; upon taking out the stoppers the morning after the battery had been charged, the liquid rose in the air-tube one-fifth of the gaseous volume. I now closed it again and examined it three days afterwards; a very curious effect had taken place; the volume of the gas in the air tube which had previously contracted had now *increased*, and it continued slowly increasing day after day. I at first believed that the nitrogen was decomposed, but after many conjectures and experiments found that the increase was due to the addition of hydrogen, a fact to me more extraordinary than the decomposition of nitrogen would have been. On repeating the experiment with nitrogen instead of air the same effect took place, but of course without the previous contraction. I now returned to battery fig. 4; several of these cells charged, some with atmospheric air and hydrogen, and others with nitrogen and hydrogen, did not exhibit the effect, though suffered to remain six weeks, each in closed circuit.

To ascertain whether the vacuum formed by the abstraction of oxygen from the liquid had anything to do with the above effect, a central narrow tube, open at both ends, was substituted for the stopper in the battery fig. 8; the hydrogen was still evolved. Not to detail a tedious set of test experiments, I at length found that two

points were essential to obtaining the effect with certainty; first, the exclusion of any notable quantity of atmospheric air from solution; and secondly, great purity in the hydrogen. In the former case, when the hydrogen could find oxygen to combine with, it was not evolved; in the latter, there would be mixed or rather diluted gas on both sides, and the forces would be balanced; thus I have never succeeded in obtaining the effect in the open battery, fig. 4, with hydrogen obtained in the ordinary way from granulated zinc or iron filings, but have sometimes succeeded with hydrogen procured by electrolysis. In the battery fig. 8, I have succeeded in producing the effect, but in a feeble degree, from hydrogen obtained in the common way, but have never failed with hydrogen obtained by electrolysis. Oxygen of the greatest purity, voltaically associated with nitrogen, does not produce a similar effect. The above unexpected results render it necessary, in order to ensure accuracy in the eudiometric experiment 24, either purposely to use common hydrogen in the batteries figs. 4 and 12, or what is more expeditious and accurate, to use a battery similar to fig. 8, but with tubes longer in proportion to their width; and having first charged the tubes with hydrogen and atmospheric air, to allow these to remain in closed circuit until all the oxygen is abstracted and a little hydrogen added, by the electrolytic effect, to the residual nitrogen; then to substitute oxygen for the original hydrogen, which will in its turn abstract the hydrogen from the nitrogen and leave only pure nitrogen. I have frequently done this with perfect success.

Experiment 30.—Hydrogen and carbonic acid in battery fig. 8 produced the same effect. The volume of the carbonic acid was increased, and hydrogen was found to have been added to it. The effect therefore is not due to any peculiarity of nitrogen, but yet some gas is necessary, for experiment 28 proves that hydrogen alone will not decompose water. I need scarcely say, that when the above-mentioned effect took place an interposed galvanometer was deflected, but the current was much too feeble to decompose iodide of potassium.

I have tried, associated with hydrogen in battery fig. 8, carbonic oxide, olefiant gas, protoxide of nitrogen, and deutoxide of nitrogen; the two former produced no current or chemical effect, the two latter gave a current and were decomposed. The volume of the deutoxide contracted one-half, this was found to be nitrogen, which thenceforth was gradually increased by hydrogen. The volume of the protoxide did not undergo the previous contraction, except slightly from solubility, but its change of state was denoted by the absorption of hydrogen in the associated tube.

I likewise tried the effect of a vacuum and hydrogen, by charging a battery (fig. 8) with 1 cubic inch oxygen and 3 cubic inches hydrogen; the current was much enfeebled by the resistance offered by the vacuum, at first iodide of potassium was decomposed and the galvanometer needle whirled round. After twenty-four hours the galvanometer needle was only deflected 10° , thus a physical was opposed to, and resisted, a chemical force; the current however continued, and all the gas in the oxygen tube disappeared, except a minute bubble; this was probably nitrogen from the atmo-

spheric air in solution, which had escaped to fill the vacuum. When the stopper was taken out the liquid rose suddenly in the hydrogen tube 2·2 cubic inches, giving the equivalent of the oxygen in the tube and in solution. It is very possible that this experiment repeated might sometimes exhibit an evolution of hydrogen in the oxygen tube arising from the escape of the nitrogen of the atmospheric air in solution, and acting as in experiment 29, but I have not seen this effect take place. It should be distinctly understood, that in all the experiments mentioned in this Postscript, except the first part of experiment 28, *single* cells only were used.

Upon the theory of the experiments 29 and 30 I will venture no positive opinion. That gaseous hydrogen should *abstract oxygen from hydrogen*, without the latter forming any other combination, is a fact so novel, that any attempted explanation is likely to prove premature. If, contrary to the views of DALTON, we suppose that gases when mixed are held together by a feeble chemical affinity, then we may say that the affinity of the nitrogen or carbonic acid for hydrogen produces the effect; the affinity of the oxygen of the water, being balanced between the hydrogen in the liquid and that in the tube, would enable the resultant feeble affinity of the nitrogen for hydrogen to prevail; but on this supposition, why does not oxygen produce an analogous effect? Its tendency directly to combine with platinum may indeed be regarded as an opposing force, but this tendency is by many considered hypothetical. On the other hand, it may be called an effect of contact; but this, unconnected with a chemical theory, presents no other idea to the mind than the fact itself presents, it furnishes no link by which we may extend the phenomena. I therefore, until a better theory be found, should be inclined to adopt the former view, and to regard mixed gas as in a state of feeble chemical union, the more especially as throughout nature we find no absolute lines of demarcation, though for conventional reasons we are obliged to adopt them; there must be many cases in which it is difficult, if not impossible, to draw the line between mechanical mixture and chemical combination.

In conclusion, I would say with regard to the whole of the experiments contained in this paper, that a longer time and more experience may give positive results in cases where I have only obtained negative ones; it is far from impossible that since curious solid combinations are formed by slow electrical currents, as in the experiments of CROSSE and BECQUEREL, so novel gaseous or liquid products may be obtained by the long-continued voltaic action of gases and liquids. This time alone can show.

For previous experiments and theories on the combination of gases by platinum, I may refer to DÖBEREINER's paper, *Phil. Mag.* Oct. 1823, in which I find he expresses an opinion that it is a voltaic effect; to the papers of DULONG and THENARD, *Annales de Chimie*, tom. 23 and 24, and to FARADAY's *Experimental Researches*, Series 6. The various experiments on polarized electrodes of RITTER, FARADAY, DE LA RIVE, BECQUEREL, MATTEUCCI, and SCHENBEIN, are also in point.