On the Action of Voltaic Electricity on Alcohol, Ether, and Aqueous Solutions. By ARTHUR CONNELL, Esq., F. R. S. E.

(Read 27th April 1835.)

I WAS led into the following train of investigation from observing, that, when minute quantities of certain substances were dissolved in alcohol, and the liquid was acted on by a moderate voltaic power, evident signs of decomposition were exhibited by the evolution of elastic fluid at the negative pole. In investigating the nature of the changes produced, I was farther led to examine the action of voltaic electricity on a variety of alcoholic solutions, and also the agency of more powerful galvanic batteries on pure alcohol and on ether; and, ultimately, I was conducted into a field, into which I should have hesitated voluntarily to enter, namely, the voltaic decomposition of aqueous solutions, which has recently been investigated with so much success by a distinguished cultivator of science. In the following paper, it will be my object to give some account of the experiments which I have made on these different subjects, and of the results and views to which I have been led. I shall begin with the voltaic action on alcohol and ether, and as I hope to be able to draw some conclusions bearing on the various theories which have been formed as to the intimate nature of these fluids, it will be necessary that the experiments made on them shall be detailed with considerable minuteness, as it is only by a very careful consideration of the experimental results, that the validity of the conclusions can be judged of.

I. Voltaic Action on Alcohol.

I found, then, that when alcohol (sp. gr. .830), having about $\frac{1}{300}$ part of pure caustic potash dissolved in it, was acted on by

the voltaic pile, the poles employed being of platinum foil, and approached to one another in an open vessel, gas was evolved from the negative pole, whilst none whatever appeared from the positive foil. A moderate voltaic power, such as a small battery of fifty pairs of two-inch plates, was amply sufficient to produce this effect. This experiment immediately recalled to my recollection a statement made a year or two ago by Dr RITCHIE,* that when alcohol, not holding any substance in solution, was acted on by a powerful galvanic battery, gas was evolved from the negative pole, whilst none appeared from the positive, and that the gas thus evolved was olefiant gas ; on which idea Dr RITCHIE concluded that the alcohol had been resolved into olefiant gas and water. As there was apparently a considerable analogy between the two observations, I was naturally led to conjecture that the gas evolved at the negative pole in my experiment, was olefiant gas ; but an examination of it soon satisfied me that this was not the case. The gas was collected simply by bringing the negative foil under a tube filled with alcohol, holding about $\frac{1}{400}$ part of potash in solution, and inverted in an evaporating basin containing the same liquid ; the power employed being sometimes fifty pairs of two-inch plates, and in other instances, seventy pairs of four-inch plates. No gas was evolved from the positive pole. A small portion of the gas collected from the negative pole was mixed with three times its bulk of chlorine, and the mixture left in a dark room over water. In the course of a few hours, an absorption had taken place to the amount of the chlorine employed, without the least appearance of the formation of oily matter : and no farther absorption occurred in twenty-four hours. The residual gas was inflammable. In short, the chlorine had left the original gas unchanged, which was therefore not olefiant gas. I then proceeded to examine it in the usual way in the voltaic eudiometer, and, after repeated and careful trials, fully satisfied

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* Phil. Trans. 1832.

myself that it consisted of somewhat variable proportions of hydrogen and of atmospheric air, or rather of the constituents of atmospheric air in relative quantities, also somewhat variable. The conclusion which I drew from this result was, that the gas evolved from the negative pole under the proper galvanic influence, was pure hydrogen, and that the oxygen and azote had been simply held in solution by the alcohol, and had been liberated along with the hydrogen in the manner which is known to occur when a gas is passed through a liquid holding another elastic fluid in solution.

Accordingly, I found that when the experiment was made without the contact of atmospheric air in a close tube, as Fig. 1, the proportion of atmospheric air mixed with the hydrogen was much diminished; and by acting on only a dram and a-half of fluid inclosed in a small tube, Fig. 2, and exposing the liquid, before commencing the galvanic action, to the vacuum of an air-pump, to separate the common air, I obtained a gas which, when mixed with half its bulk of oxygen, and fired by the electric spark, left no sensible residue after the explosion, and was therefore pure hydrogen. By placing the foils side by side in the manner done in this latter experiment, the quantity of gas liberated is considerably increased.

Precisely the same result was obtained by employing alcohol of sp. gr. .7928, at 66°F., as had been got with alcohol of sp. gr. 830. A dram and a-half of alcohol, sp. gr. .7928, having in solution from $\frac{1}{200}$ to $\frac{1}{250}$ of potash, yielded, when acted on in the tube, Fig. 2, by seventy pairs of four-inch plates, the poles being of platinum foil, and placed side by side at a short distance, a cubic inch of gas from the negative pole in less than a quarter of an hour, and $2\frac{1}{2}$ cubic inches in $2\frac{1}{4}$ hours from the commencement. The action was so intense, that the liquid boiled in a short time, although the lower part of the tube was kept plunged in cold water. The liquid also acquired a reddish colour soon

after the commencement of the action and some white matter collected by degrees at the bottom of the tube, which proved to be carbonate of potash. The gas was found to be pure hydrogen. The reddening of the solution was due to the formation of some resinous matter, which is obtained when the liquid is afterwards mixed with a little water, and concentrated by evaporation.

Several circumstances tended to shew, at an early period of these researches, that the true nature of this action consisted in the decomposition of water contained in the alcohol, apparently as a constituent where absolute alcohol was acted on ; the hydrogen being evolved at the negative pole, and the oxygen not appearing, from being employed in producing certain secondary effects. I found that there were several ways in which gas might be made to appear at the positive pole also. If alcohol considerably diluted, as with an equal bulk of water, or a little more, was acted on, a very feeble evolution of gas was observed from the positive pole, but quite insignificant compared to that from the negative. If the alcohol was stronger, as .835 or .840, and the proportion of potash was a little increased, as for instance if about $\frac{1}{100}$ potash was dissolved, then a slight effervescence ensued from the positive pole ; and there was in general a greater tendency to an evolution of gas, when platinum wires were used as poles, than when foils were employed. A singular influence on the result was also observed to be produced by the nature of the vessel employed for containing the solution. Thus, if alcohol, sp. gr. .830, with $\frac{1}{200}$ of potash dissolved, was acted on in a vessel of glass or porcelain by platinum foil poles, it shewed, as usual, the effervescence at the negative pole, and none from the positive ; but if the experiment was performed in a vessel of platinum, a feeble stream of bubbles was seen to rise from the positive pole also, but trifling compared to the negative gas. The same effect was produced by such other metallic vessels as I tried, which were those of silver, lead, iron, and copper. A simi-

lar appearance was observed in certain other equally singular circumstances. If, after the action had been going on for a few minutes in a glass or porcelain vessel, the poles being of platinum foil, the action was stopped by removing one of the wires from the battery, and when gas had ceased to come, the poles were reversed, the foil which before had been negative being made positive, and the former positive made negative, then a few bubbles arose for a minute or two from the positive foil, with the usual effervescence from the negative ; and this might be repeated, after a sufficient interval, as often as was thought proper. The only explanation I can offer of these curious appearances is, that the negative foil, when suddenly made positive, still retains for a short time some portion of its former negative character, and therefore exerts a kind of repulsive action on the electro-negative substance the oxygen, at the very time when the electric current is determining its passage to the positive side of the pile. The action of the metallic vessels seems more difficult to explain, the property being possessed as well by electro-positive metals as by those of an electro-negative character ; but probably depends on some peculiar electric influence exercised on the constituents of the alcohol, by which they are rendered less disposed to combine with the nascent oxygen.

These different modifications of the phenomena do not, however, I conceive, affect the constant nature of the action. The evolution of hydrogen from the negative pole is invariable, and the determination of oxygen to the positive pole I apprehend to be equally so, the only variation being in the circumstance of its being *visible* or not.

Before, however, attempting to develope this view farther, I wish to state the electric action on alcohol, holding small quantities of other bodies than potash in solution, and on pure alcohol.

I found that similar quantities of several other substances, soluble in alcohol, produced analogous effects to potash. Thus, when small quantities of chloride of calcium, of nitrate of lime,

of iodide of potassium, of boracic acid, of arsenic acid, and of some other bodies, were dissolved in alcohol, hydrogen was evolved, as in the case of potash, from the negative pole, whilst none appeared at the positive pole ; but in these cases the action was not so great as with potash. Thus, from $1\frac{1}{5}$ dram alcohol, containing about $\frac{1}{500}$ of recently ignited chloride of calcium, and acted on in the tube Fig. 2 by seventy pairs of four-inch plates, about one-third of a cubic inch of gas was obtained in half an hour. The negative foil then became coated with lime, and the action was almost entirely stopped ; but it was again renewed on removing the coating from the foil, and one-sixth of a cubic inch more gas was got in from two to three hours. I shall afterwards notice more particularly the nature of the changes produced on the substances held in solution, when they appear to be decomposed.

Alcohol holding a little iodine in solution shewed no effervescence from either pole, when acted on by fifty pairs of two-inch plates, a power amply sufficient to shew the action with the other substances.

My next object was to endeavour to obtain a voltaic action on alcohol not holding any foreign body dissolved. The strongest galvanic power which I had at my command consisted of 216 pairs of four-inch plates ;* and this power I found sufficient for my purpose. The alcohol acted on was placed in the tube Fig. 2, of the capacity of $1\frac{1}{5}$ dram. The platinum foil poles were about one inch long by one-fifth broad, and were soldered with gold to platinum wires, of about $\frac{1}{40}$ inch diameter, which passed through the cork. The bent tube served for collecting the gas. The

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* All the galvanic batteries employed in the experiments detailed in this paper were fixed in mahogany troughs in the usual way. The charge employed was two measures of sulphuric acid, one measure of nitric acid, and about 100 measures of water.

alcohol acted on had the specific gravity of .7928 at 66° F.* To produce a proper action, it was generally necessary to bring the foils within one-twentieth or one-thirtieth of an inch of one another, although sometimes the effect took place at the distance of one-tenth. An evolution of gas was observed to begin sometimes almost immediately, and in other instances after the lapse of a minute or two, the difference in this respect, as well as in the requisite proximity of the foils, depending on the state of action of the battery, and the perfection of the various metallic connexions.

When action was obtained with the foils, at the distance of one-tenth of an inch, it was easy to observe that the gas came from the negative pole, none being liberated from the positive pole. The action was so intense, that the liquid soon began to boil, and this increase of temperature materially contributes to the decomposition which ensues. The gas was collected sometimes over water, and sometimes over mercury, the volatilized alcohol passing over at the same time, and condensing. The quantity of permanent gas liberated was small, from .2 to .3 of a cubic inch being collected in about an hour; and there was a limit to the quantity collected, arising from the boiling of the alcohol, which left the foils partly uncovered, as well as from the diminished action of the battery.

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* I obtained the alcohol of this specific gravity by Mr GRAHAM's process of exposing alcohol .830 to the vacuum of an air-pump with quicklime, the exposure being continued for some weeks, and the lime, which was common building quicklime, being renewed during the process. I could not get it of lower specific gravity. The specific gravity of .7928 at 66° F. appears, by MEISSNER's table, to correspond with .795 at 60° F., and with .792 at 68° F., or 20° C. In this country, absolute alcohol is usually reckoned to have a specific gravity of .796 at 60° F.; and on the Continent it is held to be of .791 at 20° C. MEISSNER, while he gives this latter as the specific gravity of absolute alcohol, states that the alcohol from grain, which is that used in this country, cannot be carried below .792 or .793.—*Gmelin's Handbuch*, ii. 276. The difference is in all probability due to the presence of a little of the volatile oil which grain and potato spirit contain.

The gas thus collected from the negative pole was examined both by chlorine and in the voltaic eudiometer, and was found, on repeated trials, to be hydrogen. There was usually mixed with it about one-ninth of common air or its constituents, derived, as in the former instance, from the liquid, and partly also, perhaps, from the water over which it was collected, when water was used for that purpose.

The alcohol acted on acquired a peculiar ethereal odour ; but I could not find that any farther change was produced on it than the admixture of a minute quantity of a yellow resinous matter, which was observed by mixing it with a little water, and evaporating nearly to dryness.

Although a battery of considerable energy is required, when it is intended to collect the gas evolved from pure alcohol, still it is possible to observe the action with smaller powers. Thus when alcohol .7928 was acted on by seventy-two pairs of four-inch plates in the tube Fig. 2, with foils parallel to one another, and from one-twentieth to one-thirtieth of an inch apart, gas was observed to arise in the course of one or two minutes ; but the quantity was much less than with the greater power, and the liquid got only moderately warm and never boiled. Even with fifty pairs of two-inch plates, and the foils at the above distance, a minute stream of bubbles could be sometimes observed with a lens after action for a minute or two. With the foils one-tenth of an inch apart, alcohol of .830 shewed no action in the cold with this power, but when heated nearly to boiling and then acted on, a slight effervescence could be observed from the negative pole.

It is essential, however, that the foils be placed parallel to one another, as described in these experiments. If they were simply approached to one another horizontally, in an open vessel, I did not observe any action on pure alcohol even with the power of 216 pairs.

It is now time to recur to the nature of the changes which I conceive to take place during this agency ; and I am the more

anxious to endeavour to establish fully the view which I have taken of the nature of the action, from the obvious bearing which it has on the intimate constitution of alcohol. The essential change appears, as already stated, to consist in the decomposition, by the direct agency of the voltaic current, of water contained in the alcohol, and apparently entering into its constitution where absolute alcohol is acted on, the hydrogen being liberated at the negative pole, and the oxygen being employed in producing certain secondary changes in the liquid, and, therefore, not appearing at its proper place. In order to pave the way for understanding this view, it is necessary to recall to recollection the strong affinity which alcohol or its constituents have for oxygen, and the variety of circumstances under which we know that an oxidation of alcohol ensues, as well as the variation on the nature of the products, according to the energy of the oxidating circumstances. The most familiar example is in the acetous fermentation, whether it takes place under the ordinary circumstances, or be accelerated by platinum powder, in DÖBEREINER'S process, the effect being truly an absorption of oxygen, and consequent formation of water and acetic acid, by oxidation of the constituents of alcohol. Another example is afforded by the action of nascent oxygen proceeding from oxide of manganese and sulphuric acid, the oxidation being in that case of a more powerful description and a more highly oxygenated acid, the formic being produced at the same time with the acetic. A third instance I had occasion to point out a year or two ago,* in which the disposing affinity of potash was sufficient to lead to the absorption of oxygen, from the atmosphere, by alcoholic solutions of potash, and to an oxidation sufficiently energetic to occasion the formation of formic as well as of acetic acid, and some resinous matter. By the agency of glowing platinum also, with access of air, ether and

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* New Edinb. Philos. Jour. April 1833, vol. xxviii. p. 231.

alcohol are oxidated, and a liquid results which has been called the lamic acid, and which, in addition to acetic acid, contains, as I also had occasion to show, formic acid, to which its reducing properties are owing.*

Now, in the action of voltaic electricity on absolute alcohol, holding $\frac{1}{250}$ part of potash in solution, I have stated that hydrogen was evolved at the negative pole, and that a yellow resinous matter resulted, and a precipitation of carbonate of potash ensued.† These changes appear to be of the same character as those which result from the spontaneous absorption of oxygen by a strong solution of potash in alcohol, the differences being, that in the latter case the oxygen is derived from an external source, and the products of the oxidation are, besides the resinous matter, acetic and formic acids; while, in the former instance, the oxygen comes from the liquid itself, by the decomposition of water under the electric agency, and the products of the oxidation are the resinous matter, carbonic acid, and probably water. The latter, in short, is a still more energetic oxidation than the former, for carbonic acid is a more highly oxidated body than either acetic or formic acids, and if alcohol or ether were oxidated to the utmost possible pitch, the products would be carbonic acid and water. The oxidating power here is not only the disposing affinity of the potash, but the presence of nascent oxygen arising from decomposing water, and the operation of these causes is greatly promoted by the great elevation of temperature attending the action.

Accordingly, I have not been able to ascertain that carbonic acid is a product in the other cases of electric agency which I have mentioned, where so powerful a disposing affinity is not in action as when potash is present. I examined the gas liberated

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* New Edinb. Philos. Jour. April 1833, vol. xxviii. p. 231.

† Such a weak solution suffers no *spontaneous* change in the same time, even with contact of air.

from pure alcohol, under powerful galvanic agency, and collected over mercury, without discovering any carbonic acid in it. The only secondary product I observed in that instance was a minute quantity of resinous matter.

Nor is it always easy to observe the formation of carbonic acid, even where potash is present, when the galvanic action is less energetic, from not placing the foils side by side, or from using a smaller power. Thus, where alcohol .802, with $\frac{1}{250}$ of potash, was acted on by thirty-six pair of four-inch plates in the tube, Fig. 3, it was only after many hours' action that I got traces of carbonate of potash, the liquid acquiring also a pale yellow tint from the formation of resinous matter. It is in such circumstances of energetic agency as those formerly mentioned* that the true nature of the action is best seen.

I formerly mentioned the occasional appearance of gas at the positive pole, either when very dilute alcohol was acted on, or under peculiar circumstances, when alcohol of greater strength was employed. This gas I have assumed to be oxygen, from the circumstance of its appearing most readily when the alcohol was weakest, and from the whole bearing of the phenomena leading to the conclusion, that water was the immediate subject of the voltaic decomposition. My attempts to collect this gas proved all unsuccessful. In a platinum vessel, although a little gas, as already stated, was evolved from the positive pole, yet, in attempting to make it pass up into a tube, the very fine stream was gradually absorbed by the liquid, and nothing collected. I expected to be more successful by acting on alcohol of moderate strength, containing a rather larger proportion of potash dissolved. Alcohol sp. gr. .838 at 60°, having $\frac{1}{100}$ of potash dissolved, was acted on in the tube Fig. 4, the poles being platinum wire, and the wire A made positive by a power, in one experiment of

fifty pairs, and in another of 100 pairs of two-inch plates. The gas arising from the positive wire was observed to consist partly of a very fine stream of gas coming from the upper part of the wire, and partly of rather larger bubbles originating at the bottom of the wire, and increasing a little in size as they ascended, by running together. The fine stream never reached the top of the tube, being gradually absorbed by the liquid. The larger bubbles collected by degrees ; but although the action was continued for above an hour, the quantity of permanent gas which was obtained was only .01 of a cubic inch, and, on examination, proved to be azote. Its origin is very manifest. The minute quantity of oxygen evolved at the positive pole, liberated along with it, as usual, some of the common air held dissolved in the liquid ; and in ascending, and partly also probably after gaining the top, the oxygen was absorbed by the liquid, the azote only remaining. I tried also to separate the positive gas from solutions of chloride of calcium and of boracic acid in alcohol of .838, thinking that such solutions would exercise a less powerful absorptive action on oxygen ; but the whole agency in such cases was so much diminished, that, in the case of chloride of calcium, amounting in different experiments to $\frac{1}{50}$ and $\frac{1}{25}$, a very feeble stream only appeared from the positive wire, and in the case of boracic acid amounting to $\frac{1}{50}$, no positive gas was evolved at all.

The evidence, however, from the whole phenomena of the various experiments which have been detailed, appears to me to be quite sufficient to shew, that the action consists essentially in the decomposition of water by the immediate electric agency, and I had fully made up my mind that such was the nature of the action before the appearance of Mr FARADAY'S paper describing the voltaic arrangement, to which he has given the name of the Volta-electrometer. It then, of course, immediately occurred to me, that that arrangement afforded the means of bringing additional evidence in support of the view which I have taken.

Before applying it to this purpose, I thought it right to investigate the principles on which it was founded, and the degree of confidence which might be placed in its indications, and I shall afterwards have occasion to allude to this subject more particularly. In the mean time I shall only observe, that I have fully satisfied myself of the accuracy of Mr FARADAY'S view, that when the same electric current passes through two different aqueous solutions, and exerts a decomposing agency on the water of these solutions, the quantity of that liquid decomposed in each solution will be exactly the same ; and hence, conversely, when the same quantity of hydrogen and oxygen, or of one or other of these gases, is evolved from two different fluids by the passage through them of the same current of electricity, we have strong grounds for concluding that in both cases water is the subject of decomposition.

In applying these principles to the present case, I employed tubes having platinum wires cemented into them by the blow-pipe, and terminated by pieces of platinum foil of one inch long by one-fifth broad, soldered with gold to their extremities. Two of these tubes were filled with the alcohol under examination, and inverted in a small evaporating basin ; whilst two others were filled with the aqueous liquid with which the alcoholic fluid was compared, and inverted as the others. These tubes were then connected as in Fig. 5. Occasionally, also, the alcoholic liquid was placed in the tube A of Fig. 6, having a wire cemented at N, and another passing through a cork at P ; and this tube was connected with those containing the aqueous liquid, as in Fig. 6.

The experiments were made on alcohol of specific gravity .802, and also of specific gravity .796. The vessel A, Fig. 5, with its tubes was filled with alcohol of the former specific gravity, holding in solution $\frac{1}{200}$ of potash ; and water acidulated with $\frac{1}{12}$ of sulphuric acid was placed in B. The tube P of the vessel B was connected with the positive pole of a battery of thirty-six pairs

of four-inch plates ; and the tube N of the vessel A was connected with the negative pole of the same battery ; the other two tubes being connected with one another by a short copper-wire. The same electric current thus traversed both solutions. Gas slowly collected in all the tubes except the positive tube of the vessel A, containing the alcoholic fluid ; and after an action of an hour and three-quarters, the negative tube of A contained .3 of a cubic inch, and the negative tube of B .35.

The experiment was repeated, placing alcohol .802 with $\frac{1}{250}$ potash dissolved in A, and water with $\frac{1}{30}$ potash in solution in B, the same galvanic power being employed. The gas in the two negative tubes increased very uniformly, and in one hour and fifty minutes, there was found in the negative tube of A .32, and in that of B .34. Both gases were analyzed by the electric spark, and were found to be hydrogen ; that from the alcohol containing mixed with it, as I was fully prepared to expect from the result of former experiments, from one-fifth to one-sixth of common air, or rather of azote, derived from the alcoholic fluid, a corresponding portion of hydrogen having doubtless been absorbed by the liquid.

Thus, then, we see, that as nearly as possible the same quantity of hydrogen was evolved by the agency of the same current, whether the liquid acted on was water or alcohol ; and I therefore conclude, on the principles of the Volta-electrometer, that in reality water was in both cases the subject of decomposition, an equal portion of it being resolved into its elements in both vessels.

Similar results were obtained with alcohol, specific gravity .796 at 60° F., having in solution, in different trials, small quantities of potash, of iodide of potassium, and of fused chloride of calcium. These different solutions were always compared with water holding the same quantity of the same substance in solution, the alcoholic solution being sometimes placed in the tubes of one of the vessels of Fig. 5, and sometimes in the bent tube A of Fig. 6,

the power employed being usually thirty-six pairs of four-inch plates. On the first influence of the current, the negative gas from the aqueous solution sometimes increased a little faster than that from the alcoholic liquid, but the quantities were not very long in becoming equalized. When the same current was made to pass through alcohol of .796, holding $\frac{1}{100}$ of iodide of potassium in solution, and water holding the same quantity of that substance dissolved, the negative tube of the former liquid was found to contain in three-quarters of an hour .11 of gas, and the negative tube of the latter .13. In a similar trial, in which one-fiftieth of chloride of calcium was the dissolved body, each negative tube contained .037 of gas in the same time. The results with $\frac{1}{250}$ of potash closely corresponded with those already stated as to alcohol of .802, the negative gas of the alcoholic solution collected in the tube A of Fig. 6, being in an hour and fifty minutes .33, and that of the aqueous .37 in the same time; and in another trial the proportions were very similar. The negative gases, when examined, were always found to be hydrogen, that from the alcohol being as usual mixed with a small variable proportion of common air or azote. In one instance I found this mixture to amount to about one-fourth part; an equivalent absorption of hydrogen having without doubt occurred.

The various experiments which have been detailed, leave, I conceive, no doubt that water is truly the subject of the direct agency of the voltaic current transmitted through alcohol. Where the alcohol is concentrated, and holds no foreign matter in solution, the quantity of water decomposed even by a powerful stream is small, owing to the indifferent conducting power of the liquid. The effect on the needle of the galvanic multiplier when a stream of moderate power, as from fifty pairs of two-inch plates, was transmitted through absolute alcohol, was very trifling, but still perceptible. The galvanometer employed was of the original simple construction, consisting of a single magnetic needle, seven inches long, and suspended by silk fibres, in the centre of

a coil of about thirty circuits of insulated copper wire ; * and its indications were quite sufficient for my purpose, as my principal object was to detect such electric currents as might be the cause of chemical decomposition, and not more trifling streams, if such exist. When the current was powerful, as from 216 pairs of four-inch plates, the effect was considerably more marked, although still limited. When, however, minute quantities of certain soluble foreign bodies, particularly of potash, were added, the conducting power was much augmented, as was shewn by the increased action on the galvanometer, and by the great increase in the decomposing action. I have already shewn that $1\frac{1}{3}$ dram of absolute alcohol yielded with difficulty .2 or .3 of a cubic inch of hydrogen in an hour's action of the power of 216 pairs ; whilst the very same alcohol, with only $\frac{1}{250}$ of potash dissolved, and with a power of seventy-two pairs, yielded one cubic inch of gas in one-fourth of that time.

It is remarkable how minute a quantity of potash is capable of causing symptoms of decomposition to be seen in alcohol, under circumstances where otherwise it cannot be observed. Thus, if absolute alcohol be acted on in a watch-glass by a power of fifty pairs of two-inch plates, by simply approaching the platinum foil poles to one another horizontally, no action whatever is observed when the alcohol holds nothing in solution ; but the presence of even $\frac{1}{8000}$ part of potash renders a minute stream of bubbles visible from the negative pole.

I formerly mentioned, that, when a solution of iodine in alcohol is acted on by a moderate power, no symptoms of decomposition are observed. The effect on the galvanometer is, however, increased by the presence of the iodine.

* I compared the indications of this galvanometer with those of two astatic sewing needles, each two inches long, one of which was placed in the centre of a coil of twenty circuits, and found the indications of the long needle fully the more delicate.

II. *Voltaic Action on Ether.*

I have given this title to the experiments made with ether, although nearly the whole of them gave negative results. The ether acted on was rectified, first by agitation with water, and then by careful distillation from chloride of calcium, and possessed all the properties of pure ether. From the powers of ether as a solvent being greatly more limited than those of alcohol, the former presents many fewer opportunities of studying the influence of the solution of foreign bodies on the voltaic agency. It is usually said that ether is capable of dissolving a minute quantity of potash; but I found the quantity taken up to be very insignificant. The ether containing this scarcely perceptible quantity was acted on by fifty pairs of two-inch plates, but no symptoms of change were observed. Results equally negative were obtained with a moderately strong ethereal solution of corrosive sublimate, and also with ether holding in solution as much dry chloride of platinum and as much dry chromic acid as it was capable of dissolving. Neither was any effect on the galvanometer observed with these liquids when they were acted on by the power of fifty pairs of two-inch plates. A dram of ether holding a few drops of bromine in solution, caused a slight deviation of the needle with this power; but no evolution of gas from either pole or other symptom of decomposition was noticed.

The action of the power of 216 pairs of four-inch plates was next tried on pure ether, in the tube, Fig. 2, both when cold and when heated near its boiling point; but no evolution of gas or other symptom of decomposition whatever was observed, although the action was continued for six or seven minutes; nor was the galvanometer affected.*

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* This experiment was made with the long needle formerly mentioned. What might be the effect on a more delicate instrument I do not pretend to say.

In none of these experiments, therefore, was there the least appearance of those indications which led to the conclusion of the existence of water in alcohol; and it would appear, that, if the results were sufficient in the one case to warrant that conclusion, the experiments with ether equally justify the contrary inference, that water does not enter into the constitution of the latter fluid. If water existed as *such* in ether, I have little doubt, from the example of alcohol, that it would have yielded to the decomposing influence of the pile, and that we should have observed the evolution of at least one of its constituents; but in none of the analogous circumstances was such an indication observed.

III. *Some general considerations on the intimate Constitution of Alcohol and Ether.*

Every one knows that the elements of alcohol are in such proportions, that, when taken in conjunction with the specific gravity of its vapour, it may be represented by one volume of olefiant gas and one volume of the vapour of water condensed into one volume; and in like manner, that ether may be represented by two volumes of olefiant gas and one volume of aqueous vapour condensed into one volume. But it is one thing to say that these fluids may be thus represented, and another and a very different thing to hold that olefiant gas and water actually enter into their constitutions *as such* in these proportions. We at present know so little of the manner in which the ultimate elements of those substances which occur in or result from organic nature are united, that it is only with great caution that special views of their mode of combination should be received. Of late a great disposition has been manifested, particularly on the Continent, to adopt such particular views, and to express the constitution of those substances more closely allied to organic

bodies, by what are called rational formulæ. The principal recommendation of this method consists in the greater clearness which it introduces into our ideas of the relative constitution of such substances ; but undoubtedly there is the greatest possible risk that, when not founded on grounds strictly experimental, these rational formulæ may not give an accurate representation of what really exists. We have the authority of the highest names for the application of such views to alcohol and ether ; but it is remarkable that these views, although founded on the same principle, have differed considerably in their details. GAY LUS-SAC appears to have adopted the above-mentioned view, that alcohol consists of water and olefiant gas, and ether of water and a greater proportion of olefiant gas.* BERZELIUS modified this opinion,† by assuming that a peculiar hydrocarbon C^4H^8 , which he called Etherine (Ae), having the same proportions of constituents as olefiant gas, but a greater total number of atoms, entered into the constitution of both alcohol and ether, which were both regarded as hydrates of this substance, alcohol being $Ae+2\dot{H}$, and ether $Ae+\dot{H}$. He afterwards saw cause to alter his view, and to assume alcohol and ether to be oxides of different radicles, the former C^2H^6+O , and the latter $C^4H^{10}+O$.‡ LIEBIG has adopted this latter opinion in regard to ether, but has rejected it with respect to alcohol. || He considers ether as the oxide of a hydrocarbon (E), different from olefiant gas, and represented by C^4H^{10} , and alcohol as the hydrate of that oxide ; *i. e.* a hydrate of ether. Ether is therefore $\dot{E}$, and alcohol $\dot{E}+\dot{H}$; and he has given a view of the composition of all the compound ethers and other relative substances, which is remarkable for consistency, and its strong analogy with the laws of inorganic com-

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* Annales de Chim., tom. xcv.

† Annales de Chim. et de Phys., tom. li. p. 313.

‡ Poggend. Annal. xxviii. 627.

|| Annales de Chim. et de Phys., tom. lv. p. 132.

binations. These different views, however, are rather to be considered as more or less probable *inferences* from experimental results, than as such experimental results themselves. Even the fact which they nearly all assume, that alcohol is a hydrate, is merely an inference like the rest; for, when in the process of etherification, the ultimate result is, that sulphuric acid takes water from alcohol, we cannot tell whether this water existed as such in the ether, or arose from a new arrangement of its elements by the affinities brought into play.

We are led, then, to inquire how far the researches detailed in the first parts of this paper are capable of increasing the probability of this inference, or of affording more direct experimental proof of the existence of water in alcohol? I confess I do not see how it is possible to avoid admitting that water was the immediate subject of voltaic decomposition in the experiments detailed. The hydrogen was evolved from the negative pole, in the same proportion as from water; the disappearance of the oxygen was accounted for; and, by particular arrangements, that element could even be made visible. The only remaining point, therefore, is, Is that water a constituent of the alcohol employed, or is its presence accidental? This point was investigated as carefully as was in my power. The alcohol acted on had, I have reason to believe, as low a specific gravity as alcohol from grain has ever been obtained, without decomposition,* and yet it still yielded hydrogen at the negative pole, under powerful voltaic agency, and more freely when its conducting power was improved by an insignificant morsel of potash. The legitimate conclusion, therefore, seems to be, that the water decomposed entered as such into the constitution of the alcohol acted on. I have not, however, the least wish to press this latter view farther than the circumstances may be supposed to warrant; and, if it can be afterwards shewn that it is possible to prepare alcohol which will

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* See Note, p. 321.

not shew the same appearances with powerful batteries capable of producing these effects on such alcohol as I employed, I shall be ready to admit that the question as to the nature of alcohol, remains as it was.

Assuming, however, in the mean time, that we have direct experimental proof of the existence of water as a constituent in alcohol, the next question is, With what is it combined? Is alcohol a hydrate of olefiant gas, as GAY LUSSAC supposes, or of ether, as LIEBIG maintains? Here, then, we are once more thrown into the field of inference; with this difference, however, that our speculations are no longer gratuitous; for, if alcohol is proved to be a hydrate, it must necessarily be a hydrate of something or other; and it is a legitimate subject of probable reasoning to inquire, with what the water is combined. On the whole, I incline to give the preference to LIEBIG'S view, for the following reasons.

The experiments on ether lead to the conclusion that this latter body does not contain water. Not only did pure ether resist the strongest voltaic power which was brought into operation on it, but I could not find any substance capable of giving it such conducting power as led to any action which countenanced the supposition that it contained water. Now, the view that alcohol is a hydrate of olefiant gas has always been taken in connection with the idea that ether also is a hydrate of the same body, having a less proportion of water; and I think that there is little doubt that the supporters of these two views will be less inclined to adopt one of them if the other is held to be disproved. The specific gravity of the vapour of ether, the arithmetic mean between that of the vapours of alcohol and water, evidently favours, as LIEBIG has remarked, the idea of a less intimate union, such as that of a hydrate.

The theory of etherification is also much simplified by holding alcohol to be a hydrate of ether; for we have only to withdraw an atom of water, and the ether remains ready formed, without any

change of elements ; and the antecedent formation of sulphovinic acid, which is now held to consist of sulphuric acid and alcohol, scarcely interferes with the simplicity of this view.

Strong analogical grounds would undoubtedly be afforded for the same opinion, from the composition of the compound ethers, if we had good reason for holding, with LIEBIG, that ether is the oxide of an unknown radicle. But the galvanic experiments with ether, seem to me to be rather against that view ; for it would appear that on electro-chemical grounds, such an oxide ought to give way under voltaic agency, by a separation of its electro-positive and electro-negative elements. Of such a separation, however, I obtained no indication whatever.

It may perhaps, therefore, be safer simply to regard ether as a ternary compound of its elements, and to express its constitution by an empirical formula $C^4H^{10}O$. Alcohol, on the other hand, may be regarded as a hydrate of ether, and its formula will be $C^4H^{10}O + \underline{H}$.

IV. *Voltaic Action on Aqueous Solutions.*

In the course of the preceding investigations, I was naturally led into an examination of the nature of the voltaic action on solutions of various acids, alkalies, and salts in water ; my principal object being to endeavour to distinguish between those cases in which the solvent and those in which the dissolved body was the immediate subject of the voltaic action, and thus to be better able to draw a similar distinction in the case of alcoholic solutions. In this inquiry, I was of course necessarily led to examine many of those experimental results and conclusions which have been unfolded by Mr FARADAY, in his interesting series of electrical researches ; and therefore I may be pardoned for stating such views as have occurred to me on this part of the subject, seeing that I did not gratuitously enter upon it, but was

necessarily conducted into it, by a train of investigation which, in its origin, had no reference to this particular part of the inquiry.

From the important aid which Mr FARADAY'S principle of the direct connection between the quantity and chemical action of an electric current, is capable, if well founded, of affording, in determining such questions as I had in view, this principle was, of course, one of my chief subjects of examination; and I found it necessary to endeavour to satisfy myself, in so far as regarded solutions, how far the evidence was sufficient to establish that the chemical action of an electric stream is proportional to the absolute quantity of transmitted electricity, and that a given quantity of electricity will decompose a chemical equivalent of the substances on which it acts.

For the purpose of bringing these principles to the test of experiment, Mr FARADAY has employed an arrangement to which he gives the name of the *Volta Electrometer*, of which there are several modifications, but all of them depending on the principle that the hydrogen and oxygen evolved from water under decomposition by a given electric current, are collected, and measured, and compared with the same or different elements, as the case may be, separated from the same or a different substance, which is under decomposition by the same electric stream.* Now, I have had ample opportunities of confirming experimentally the truth of the above law, in so far as regards water, and have no doubt whatever that the same current of electricity will always decompose the same absolute quantity of water, when it exerts its decomposing

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* It is only doing justice to MM. GAY LUSSAC and THENARD to remember, that they long ago employed the quantity of the gases evolved by water under the agency of the voltaic current as a measure of its chemical effects (*Recherch. Phys. Chim.*, Part i.) They did not, however, compare this quantity with other effects produced by the same current at the same time.

influence on that body. I have compared dilute sulphuric acid of a given strength, with the same acid of different strengths, with alkaline solutions, and with solutions of alkaline sulphates, by transmitting the same electric stream through them, and have found that the quantity of hydrogen evolved from the negative pole was always, with trifling deviations, a fixed quantity for the same current. The quantity of oxygen separating at the positive pole was subject to those variations from the absorption of the fluid, which Mr FARADAY has pointed out; but the quantity in one experiment with another was evidently such as corresponded with the hydrogen evolved, after allowing for the absorption.

It is evident how important an aid this principle affords us, in explaining what passes during the electric decomposition of aqueous solutions; for if, in comparing with one another, solutions of substances of different atomic constitutions, we obtain hydrogen or oxygen, or both, in the proportions contained in water, we have strong grounds for concluding that the solvent, and not the matter dissolved, has been the subject of decomposition.

Accordingly, it is in this way that we are enabled to determine, with every appearance of probability, that in a great many, perhaps in all cases of solutions of the oxyacids, water only is the subject of direct voltaic decomposition. Thus the same voltaic current was passed through dilute sulphuric acid, and a solution of boracic acid, and it was found that very nearly the same relative quantities of hydrogen and oxygen were evolved from both solutions in the same time, notwithstanding the difference in the atomic constitution of the two acids. There was, therefore, little doubt that, in both solutions, the water, and not the acid, had suffered decomposition. Iodic acid appeared to me to be extremely well calculated for such an experiment, as the feeble affinity by which its elements are held together, afforded the most favourable circumstances for a direct decomposition of an

oxyacid in solution, if such a decomposition is likely to occur. Two of the tubes (Fig. 5), formerly described, * were filled with a solution of one part of iodic acid, in about ten parts of water, and inverted in an evaporating basin. Two others were filled with sulphuric acid, diluted with twelve parts of water, and also inverted. After connecting them together, as formerly described, the current from fifty pairs of two inch plates was passed through them. Iodine separated from the negative pole of the iodic solution, without any evolution of elastic fluid from that pole. Gas was liberated from all the other poles. In a quarter of an hour, the following quantities of gas were obtained :—

	Cub. In.
In the positive tube of iodic solution, ...	.14
..... sulphuric solution, ...	.12
In the negative tube of do. do.	.33

Now, here there can hardly be a doubt that, in the iodic solution, the water only was directly decomposed, and the iodine was a secondary product, arising from the reducing action of hydrogen. Had the iodic acid been directly decomposed, the quantity of oxygen liberated ought to have been five times greater than that got from the dilute sulphuric acid, in which we already know that water is the subject of direct decomposition.

The next point of inquiry is, whether, in the case of the hydracids, water or the acid is the subject of direct electric agency ? and this question becomes one of considerable importance ; because, if the acid is directly decomposed, the experimental results obtained afford an example of the application of the principle of definite voltaic action to another substance than water, whilst, if the water is decomposed, it is only another instance applicable to that liquid. It is with considerable hesitation that I have brought myself to differ on this point from so high an authority as the first propounder of the doctrine of definite voltaic action ; and I have

only done so after obtaining what appears to me to be experimental proof that the decomposition of the hydracids is a secondary result. That hydrogen is evolved in such cases in definite quantity, there can be no doubt whatever. I have repeatedly found, on comparing dilute solutions of muriatic acid and of hydriodic acid with dilute sulphuric acid in the volta-electrometer, that the quantity of hydrogen evolved was exactly the same from all these solutions. It is the question, whether, in the case of these hydracids, the hydrogen proceeds from the acid, or from the water, that affords room for difference of opinion. Mr FARADAY contends, that it is derived from the acid, and that consequently the hydracids afford another instance of definite voltaic action. His reasons, which, at the utmost, are merely analogical, are, first, that chlorine and iodine combine with hydrogen atom to atom, as oxygen does ; and, secondly, that chlorine can be directly separated from lead, potassium, &c. in the dry state, by electric agency. The first being an argument which can only be addressed, in its full extent, to British chemists, can hardly be held to be of great weight ; and, with respect to the second, I think I shall soon make it at least doubtful whether one substance, namely, iodic acid, although it resists decomposition in solution, may not give way in the dry and fused state. But it is unnecessary to dwell longer on mere argument from supposed analogy ; for I think I can bring forward a few experiments on the hydracids themselves, which appear to lead directly to the conclusion that the evolution of chlorine and iodine during voltaic action on solutions of those acids, is a secondary result, and that the hydrogen is derived from water directly decomposed by the electric current.

Into a tube of the capacity of one and a half dram, moderately strong muriatic acid was poured, and another tube of the same size was filled with distilled water. These two tubes were connected, as in Fig. 7, by asbestos moistened with distilled water ; the asbestos having been previously washed with diluted muriatic

acid, and then thoroughly freed from all traces of acid by water. The muriatic acid was then connected with the negative side of fifty pairs of two-inch plates, and the distilled water with the positive, when a slight effervescence took place from both poles. After a quarter of an hour's action, not the slightest trace of chlorine could be detected in either tube, either by the smell or by bleaching action on test-paper, but a feeble trace of acid was shewn by test-paper in the positive tube. After an action of one hour and a quarter, there was still not a trace of chlorine in either tube, and the reddening action on test-paper of the positive liquid was somewhat increased. In nine hours, the reddening action of the water was still more decided, and a very feeble and doubtful odour of chlorine was observed in it. Now, what inference is to be drawn from this experiment. I apprehend the following is the explanation. The slight effervescence which took place from both poles, arose from decomposed water, its elements going to their proper poles. The muriatic acid was not decomposed; had it been so, the chlorine would have immediately passed towards the positive pole, and would have betrayed itself in one or both tubes by its usual characters. If, only after nine hours' action, a doubtful trace of it could be observed in the positive water, its origin was due to the secondary action of the oxygen on the muriatic acid, which had passed over partly by the natural tendency of the acid to the positive side, and partly by capillary action. That this is the true explanation, will still farther appear from the following experiments. Muriatic acid, diluted with two or three times its bulk of water, was placed in A as before, and water acidulated with a few drops of sulphuric in B, with which latter liquid the connecting asbestos was moistened. The diluted muriatic was made negative, and the acidulated water positive. A brisker effervescence than before took place from both poles, from the better conducting power of the positive liquid; but still in ten minutes not a trace of chlorine could be detected in either tube, either by the smell

or by test-paper. The battery was then reversed, the muriatic acid being now connected by the same platinum foil as before, with the positive side of the battery, and the acidulated water with the negative. A brisk effervescence took place as before from the negative pole, and a slight effervescence from the positive, and in less than two minutes, a decided smell of chlorine was evolved from the positive tube, and shortly after test-paper held close to the positive foil was bleached, and the muriatic liquid got a yellow tint from dissolving chlorine. In this experiment it is evident that, before the reversal of the poles, no decomposition of muriatic acid took place, and that the whole, or greater part, of the oxygen which was evolved before the reversal from the positive wire, was employed *after* that change in reducing muriatic acid by combining with its hydrogen and liberating chlorine. When the diluted muriatic was at once connected with the positive pole of the battery in fresh action, and the acidulated water with the negative side, the smell of chlorine was even sooner, and more distinctly observed.

In another experiment, I examined more particularly the gas evolved from the positive pole, when the muriatic acid was positive, and found it to be chlorine. A small evaporating basin containing muriatic acid diluted with twice its bulk of water, was connected with another evaporating basin containing sulphuric acid diluted with five parts of water, by asbestos moistened with the latter fluid. The negative foil was placed in the dilute sulphuric acid, and the positive foil brought under a tube filled with the dilute muriatic acid, and inverted in the basin containing the latter liquid. The gas evolved from the positive pole was shewn to be chlorine, by being gradually entirely absorbed by the liquid, and by the strong smell of chlorine which the liquid acquired.

The experiments with hydriodic acid led all to the same views, and, from the phenomena being more apparent to the senses, were even more satisfactory.

A moderately strong solution of recently prepared and colourless hydriodic acid was placed in A, and connected with the negative side of fifty pairs of two-inch plates. Distilled water was placed in B, and connected with the positive side ; and the connexion was made by asbestos, moistened with distilled water. A slight effervescence ensued from both poles. During the first ten minutes, there was no appearance of discoloration of the liquid in either tube. A slight yellow tint then appeared in the positive liquid, and no change in the negative, and shortly after, a just perceptible acid reaction on test-paper was observed in the positive liquid. In a quarter of an hour, the battery was reversed in the manner already described as to muriatic acid. Instantly, notwithstanding the diminished action of the battery, the hydriodic solution which had been previously colourless, acquired a brownish colour round the positive pole, and not a bubble of gas appeared from that pole, whilst gas rose from the positive foil. The brown colour gradually diffused itself through the liquid.

This experiment was now repeated with the difference that the level of the distilled water was made about a line higher than that of the hydriodic solution, which was perhaps a little weaker than in the preceding experiment. A slight evolution of gas soon arose from both poles, and in a quarter of an hour there was not the slightest discoloration of the liquid in either tube, nor did the water shew any acid reaction. The battery was then reversed. The hydriodic solution was immediately discoloured round the positive foil as before, without any liberation of elastic fluid, whilst there was a slight effervescence from the negative foil.

This last experiment was repeated with a power of thirty-six pairs of four-inch plates, with precisely the same result.

The explanation of these experiments seems very apparent. When the hydriodic acid solution is in connexion with the negative side, and the water with the positive, water is resolved into

its elements, but the acid is not decomposed. If it were, iodine would have immediately made itself manifest. If after ten minutes in the first mentioned experiment a trace appeared in the positive water, this was due to a small quantity of the acid itself which had passed over, and was reduced by nascent oxygen, as is evident from the acid action on test-paper which soon followed, and from the circumstance that no iodine appeared in a longer time, when precautions were taken to diminish the quantity of acid passing over. On the other hand, the instant the acid was made positive, iodine appeared, and oxygen disappeared, the latter giving rise to the former by combining with the hydrogen of the acid.

From these experiments, therefore, I consider myself entitled to conclude, that, when solutions of muriatic and hydriodic acids, and doubtless of other hydracids, in water are submitted to voltaic agency, the chlorine, iodine, or other electro-negative constituent of the acid, is a secondary product, and the hydrogen arises from water directly decomposed by the voltaic agency. This action, consequently, does not furnish an instance of definite voltaic action on the hydracids, but is merely another example of the application of that principle to water.

Questions of a similar nature arise relative to the decomposition of the haloid salts, and are also of importance; because, if chlorides, iodides, &c. are dissolved as such, and are directly decomposed by the electric current, we have, as before, an instance of definite action in regard to another class of substances than water. Mr FARADAY inclines to the affirmative of this opinion, although not with the same confidence as in regard to the hydracids. The fact is equally certain in this instance, that the hydrogen is evolved in a fixed proportion, as I have verified for alkaline chlorides and iodides; but, by a set of experiments of the same description as those detailed in regard to the hydracids, I have been led to the conclusion, that the chlorine and iodine

evolved in the case of solutions of the haloid salts also, are secondary products, and that the hydrogen arises from the direct decomposition of water.

A rather weak solution of chloride of potassium was placed in a tube of the same size as before, and distilled water in another similar tube, its level being a little higher than that of the saline liquid, and the connexion made by moistened asbestos. The saline solution was then made negative, and the water positive, by a power of fifty pairs of two-inch plates. Gas appeared in one or two minutes from both poles. In half an hour, not the least trace of chlorine could be detected in either tube by the smell or by any bleaching action on test-paper. The battery was then reversed. An effervescence took place from the negative pole, but none from the positive, and in half an hour more, notwithstanding the diminished action of the battery, a faint odour of chlorine was discerned.

In a repetition of the experiment connecting the solution of chloride of potassium with the negative side, and the water with the positive, gas soon appeared as before from both poles, and alkali was very soon afterwards detected on touching the negative foil with test paper, and acid on touching the asbestos on the positive side of the negative tube, shewing that acid was travelling towards the water in the positive tube ; but no smell of chlorine was detected. In twenty minutes a doubtful trace of acid was found in the positive liquid, but still no trace of chlorine. In two and a half hours the trace of acid in the positive tube was still slight, and a very doubtful trace of the odour of chlorine observed. In seven hours an acid reaction and a feeble odour of chlorine were quite manifest in the positive liquid ; but not the slightest trace of chlorine in the negative tube.

In these experiments it is manifest, that when the saline solution was negative and the water positive, chlorine was not liberated until acid had passed into the positive tube, so as to enable the oxygen there evolved to occasion the appearance of the

chlorine by a secondary action. When the saline solution was positive and the water negative no oxygen was evolved, but it was employed in causing the secondary appearance of chlorine which was observed at a far earlier period than when the reverse arrangement was adopted.

When water acidulated with sulphuric acid was substituted for pure water, and used for moistening the asbestos, the effects were much more marked. The saline solution was made positive, and the acidulated water negative; there was effervescence from both poles, but no smell of chlorine, or bleaching action in thirteen or fourteen minutes. The battery was then reversed, when a distinct smell of chlorine was observed in less than one minute, with slight effervescence from the positive pole and stronger from the negative, and in a few minutes more, test-paper was bleached in the neighbourhood of the positive foil.

A rather weak solution of iodide of potassium was then rendered negative, and distilled water positive, the connexion being made by asbestos moistened with water. A slight effervescence ensued from both poles. In half an hour there was not the slightest discoloration of the liquid in either tube. The battery was then reversed. Instantly the liquid near the positive foil in the saline solution was discoloured, without any evolution of gas from that pole, whilst gas appeared from the negative foil. The iodine gradually increased in the positive liquid.

These results were quite analogous to those with chloride of potassium. When the solution of the iodide was negative, and the water positive, no iodine appeared, but gas was evolved from each pole by the decomposition of water. On the reversal of the battery the oxygen ceased to come, and iodine appeared in its place by its secondary action.

The question with what substance the oxygen combines to cause the separation of the chlorine and iodine, depends on the point whether chlorides and iodides are dissolved as such, or as muriates and hydriodates. If in the former state, then the

oxygen must combine with potassium, and liberate the electro-negative constituent of the haloid salt. If in the latter condition, then it will unite with the hydrogen of the acid of the dissolved salt and liberate the other element. Either view will explain the appearance of the chlorine or iodine.

It is evident that we can easily explain, conformably to these views of the secondary origin of chlorine and other analogous substances in solutions of the hydracids and haloid salts, the greater facility with which it has been observed that some of such solutions are decomposed, than water acidulated with an oxyacid. The attraction of the element with which the nascent oxygen, or in the case of ordinary metallic solutions, the nascent hydrogen, combines, will aid the electric action; and the more feeble the existing combination of that element, the less will its union with the nascent oxygen or hydrogen be opposed, and the more will the voltaic agency be facilitated.

We can also explain, in a more satisfactory manner, on these views, that on the idea of the primary origin of the chlorine, the known fact, that in strong solutions of muriatic acid or of chlorides, chlorine separates at the positive pole with scarcely any accompaniment of oxygen, whilst in weak solutions of these bodies a mixture of these gases is liberated. When the nascent oxygen finds around it abundance of the dissolved body, it enters wholly into the new combination; but in weak solutions the overplus is liberated along with the chlorine produced. Analogous views apply to the combinations of iodine.

If the above views as to the haloid salts are well founded, it follows that the appearance of hydrogen in definite quantity in the voltaic decomposition of solutions of those salts is only, as in the case of the hydracids, another example of the definite decomposition of water.

It is therefore to the experiments on dry substances that we must look for the proof of the application of the principle to other bodies. On such substances I have made no experiments,

with this particular view, and therefore am not entitled to make any other observations on Mr FARADAY'S researches on them, than to observe that many of the experiments, particularly those with the chlorides and iodides of lead (814, 818, 794), the chloride of tin (819, 789), and the borate of lead (799), undoubtedly appear to lead to the establishment of this highly important principle with respect to other bodies than water.

We must, however, take care that we do not extend our ideas of this definite action farther than any of the experiments which have been adduced in support of it by its author will warrant, a misconception into which I have reason to believe that some who have not fully considered the evidence have fallen. One limit to it has been set, on the ground that the electric action itself is supposed to be capable of decomposing such bodies only as are composed of the same, or at least a like number of atoms of their elements, a point to which I shall presently advert. Accordingly there are no grounds whatever for holding that any definite action applies to such bodies as the great class of oxyacids and many other substances, admitted on all hands to consist of an unequal number of elementary atoms, and if such bodies are really undecomposable, no such definite action of course is possible. But, farther, there is as yet no evidence of the application of definite voltaic action to the extensive class of ordinary salts consisting of an acid and an alkali, and yet many of them are composed of a like number of chemical equivalents, and are undeniably subject to electric decomposition. According to the experiments hitherto made, the protoxides, water included, and the principal haloid salts, are the chief examples of the application of the law, and for this reason, that these are the principal substances on which the voltaic current operates.

The point to which I have just alluded, whether the decomposing agency of the electric fluid reaches only to substances composed of a like number of elementary atoms, is second only in importance to the law of definite action, and would require

very conclusive evidence before it could be adopted as a universal law.

Independently of the consideration, that, according to almost all the continental chemists, the principal haloid salts are not composed of a like number of atoms, there is at least one substance, the oxide of antimony, which Mr FARADAY found to be decomposed, in its fused state, by voltaic action, and which has been hitherto held, by the universal opinion both of British and continental chemists, to be a sesqui-oxide.* The oxide of bismuth, it is also extremely likely, is in a similar situation, according to the views on the Continent, as to its atomic constitution, which the specific heat of the metal renders very probable.

Neither does it necessarily follow, because a substance is not decomposed in solution, that it will not give way in the dry and fused state; because, if water is in its own nature more susceptible of voltaic agency than the dissolved body, the action may be limited to the solvent when the solution is acted on. Assuming potash to suffer direct decomposition in its fused state, we have no reason to suppose that it gives way in solution. Our views as to the oxyacids will therefore be taken, from experiments made on them in the anhydrous and fused state, which, however, it is not always very easy to accomplish.

Arsenic acid I could not succeed in freeing from water without decomposing it. Of anhydrous sulphuric acid I possessed too little to attempt any experiments with it.

I made some experiments on dry and fused iodic acid, which, from the slight affinity of its constituents, I thought likely to throw light on the subject.† A difficulty, however, presented it-

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* The attempts to show that it contains traces of a protoxide are evidently too imperfect to be entitled to regard, in their present state.

† The iodic acid was prepared in the usual way by the agency of nitric acid, and was several times alternately dissolved in water and evaporated to dryness, to free it from nitric acid.

self, arising from the circumstance, that, when completely freed from water, its points of fusion and decomposition are extremely near one another. I freed it from water by keeping it in a fused state, in a tube, for a considerable time after a portion of the acid was decomposed, and until water was no longer evolved. The residue was dry and hard, and was immediately transferred to a long bent and narrow tube; where platinum wires connected with the two ends of a battery of fifty pairs of two-inch plates were brought into contact with it, the before-mentioned galvanometer being also introduced into the circuit. The iodic acid was then heated to fusion by a spirit-lamp, when immediately a considerable and even permanent deflection of the needle took place. Although it was thus quite manifest that a current passed, it was impossible for me to say with certainty that the acid was decomposed by the voltaic agency, because the heat applied was itself sufficient to cause decomposition and volatilization of iodine on both sides.

I repeated Mr FARADAY'S experiment on fused boracic acid, and at first thought that I had succeeded in decomposing it. The acid was fused on platinum wire in the reducing flame of a large lamp of melted tallow, acted on by a hydrostatic table blowpipe, the voltaic power employed consisting of 216 pairs of four-inch plates. There was an evident action on the galvanometer, and sparks were visible from the fused acid. Similar results were afterwards obtained with only thirty-six pairs of four-inch plates. But, on repeating the experiment with the 216 pairs, and fusing the acid by the oxyhydrogen blowpipe, I was surprised to find that there was no action on the galvanometer. The idea which I then formed was, that the reducing action of the carbonaceous vapour of the lamp flame had aided the voltaic agency, but that in the oxyhydrogen flame, which is of course destitute of carbonaceous matter, the voltaic current alone could not produce the effect. This view, if well founded, would undoubtedly have been an example of voltaic agency, other affini-

ties aiding the action, as is known to happen in other cases. But on heating the acid strongly in the oxyhydrogen flame, and then transferring it in its pure and transparent state to the table blowpipe flame, I could get no action on the galvanometer or sparks with thirty-six pairs of four-inch plates, whilst it remained clear and transparent, although I observed both, when it became dark coloured from carbonaceous matter derived from the flame. The most probable explanation, therefore, seems to be, although the case is not free from ambiguity, that the carbonaceous matter merely gives a certain degree of conducting power to the mass, and that this is the source of the action on the galvanometer and of the sparks. I have thought it worth while to detail the results, because they may at least serve as a caution to others in making similar experiments; if they are insufficient to alter our ideas of the non-action of the electric current on this substance.

In the whole circumstances, however, I cannot help having some doubts as to the universality of the law of the necessary correspondence between voltaic decomposition and equality of atomic constitution, although I am by no means prepared to reject it altogether, and, on the contrary, think that, to a great extent, it may be well founded. It certainly appears very probable, that, when the constituent elements of substances are nearly balanced in number, and particularly when that number is small, they will be peculiarly in that state of electric opposition of character which will make them susceptible of voltaic agency; and, on the other hand, where the number of atoms is considerable and unequally balanced, the mode of combination may partake more of that character of union of which organic nature appears to present numerous instances in its ternary and quaternary combinations, and in which the electric nature of the combined elements is probably less directly opposed, and will therefore be less adapted for voltaic action, and may very probably even afford many cases where it will be altogether excluded. Feebleness of affinity in the constituent elements may, however, sometimes supply the place of simple atomic constitution,

by opposing less resistance to decomposing agency, and, on this ground, may be explained the decomposition of fused iodic acid, if that really is a case of decomposition; and it seems not unlikely that the circumstance that the oxide of antimony is easily reducible, is the reason why it is subject to galvanic action, although by no means a simple atomic compound. But I throw out these views merely as speculations on a subject which cannot be satisfactorily rested except on the sure basis of experiment.

There still remains another part of this memoir, relating to the nature of the changes produced by voltaic agency on certain of the substances held in solution by alcohol, particularly in more concentrated solutions. On this part of the subject I hope to be able to make a communication to the Society in the course of next session.

POSTSCRIPT.

Since the preceding paper was read, I have succeeded in obtaining alcohol of still lower specific gravity, by continuing the exposure in the vacuum of an air-pump with quicklime for eight weeks, and renewing the quicklime after the first week. The alcohol thus obtained had the specific gravity of .7928 at $62^{\circ}\frac{1}{5}$ F., which corresponds with .7938 at 60°F. and with .790 at 68°F., or 20°C. A portion of this alcohol submitted to the action of 216 pairs of four-inch plates in the tube, Fig. 2, the platinum foil poles being at the distance of from $\frac{1}{50}$ to $\frac{1}{40}$ of an inch from one another, still yielded gas from the negative pole, although in smaller quantity than the alcohol of sp. gr. .792 at 20°C. That the quantity of gas was smaller, was merely owing to the circumstance that the conducting power of the former alcohol was inferior to that of the latter; for the addition of the most insigni-

ficant morsel of potash caused the liberation of a comparatively speaking abundant supply of elastic fluid, and that with a smaller voltaic power. When only $\frac{1}{1000}$ part of pure caustic potash was dissolved in the alcohol of .790, and it was acted on in the tube, Fig. 2, by seventy-two pairs of four-inch plates, the foils being $\frac{1}{20}$ of an inch apart, half a cubic inch of gas was collected from the negative pole in ten minutes, and the evolution still went on. This gas was found to be hydrogen as usual. But this was by no means the limit to the operation of the alkali in giving conducting power. With $\frac{1}{2000}$ of potash in solution, this alcohol still gave a considerable stream of gas; and when this solution was farther diluted with the same alcohol, so as to leave only $\frac{1}{10000}$ of potash dissolved, the stream from the negative pole, with the power of seventy-two pairs, was scarcely diminished, and much more abundant than that from the alcohol holding nothing in solution, with the power of 216 pairs. The dilution might evidently have been carried much farther without destroying the effect of the alkali. Since alcohol of so low specific gravity thus still yielded hydrogen from the negative pole, additional confirmation is evidently afforded of the views set forth in the preceding paper, as to the intimate nature of alcohol and ether; and it appears to me that no reasonable doubt can any longer exist, that the researches which have been detailed afford experimental proof of the presence of water as a constituent in absolute alcohol, and of its absence in ether.

The Figures referred to in the preceding paper are contained in Plate XIII.