XI. *Second Letter on the Electrolysis of Secondary Compounds. Addressed to* MICHAEL FARADAY, *Esq. D.C.L. F.R.S., Fullerian Prof. Chem. Royal Institution, &c. &c. &c. By* J. FREDERIC DANIELL, *Esq. F.R.S. For. Sec. R.S., Prof. Chem. in King's College, London.*

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MY DEAR FARADAY,

YOU will not, I think, be surprised or displeased at my addressing you again upon the *Electrolysis of Secondary Compounds.* The whole of my very limited leisure, since my last Letter which the Royal Society did me the honour to publish in the Philosophical Transactions for 1839, has been occupied with experiments upon the subject; and I have obtained some results which I trust will not be found unworthy of the continued attention of yourself and the Society. The mode of investigation which I have adopted seems to me calculated not only to throw light upon the nature of electrolytes, but upon the mode in which the chemical elements group themselves together to constitute *Radicles* or *Proximate Principles*, the question which now seems universally to occupy the attention of chemists. I feel more than ever satisfied that the laws of electrolysis will be found to lead to the solution of this great problem.

Upon reflecting upon the constitution of the oxyacid salts, as developed in my last Letter, I conceived that it might be possible to obtain further evidence that the simple *cathion* travelled as a metal to the platinode, while the compound *anion* was passing in the opposite direction; and that means might be devised of stopping it, as it were, *in transitu.* Your beautiful experiment*, which I have often repeated with success, of precipitating the magnesia from a solution of Epsom salt against a surface of pure water, in the course of a voltaic current, suggested the mode of proceeding. According to my view of that experiment, the first electrolyte was resolved into the compound anion, sulphuric acid + oxygen, which passed to the zincode; and the simple cathion, magnesium, which on its passage to the platinode was stopped at the surface of water, from not finding any *ion*, by temporarily combining with which it could be further transferred according to the laws of electrolysis. At this point, therefore, it gave up its charge to the hydrogen of the water, which passed in the usual manner to the platinode; and the circuit was completed by the decomposition of this second electrolyte. The corresponding oxygen, of course, met the magnesium at the point where it was arrested in its progress, and, combining with it, magnesia was precipitated.

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* Experimental Researches, § 494.

Now it seemed to me that this combination of the oxygen and metal was a secondary result, due to the local affinity of the two elements thus brought into juxtaposition; and was in no way connected with the primary phenomena of the current, which would have completed its course whether this combination had taken place or not, i. e. whether magnesium and oxygen had been separately evolved, or whether magnesia had been formed by the combination of the two. It also seemed probable that, although in the very slow action of this experiment this combination invariably took place, by varying the experiment so as to evolve metals possessing different degrees of affinity for oxygen, and particularly by shortening the time in which the evolution might take place, instances might be found of some portion of the metal escaping this combination, which would thus afford the most incontrovertible proof of the point to be established.

I was happy enough to succeed perfectly in my first experiment: nothing could be more simple than the arrangement.

Experiment 18.—A small glass bell, with an aperture at the top, had its mouth closed by tying a piece of thin membrane over it. It was half-filled with a dilute solution of caustic potassa, and suspended in a glass vessel containing a strong neutral solution of sulphate of copper, below the surface of which it just dipped. A platinum electrode, connected with the last zinc rod of the large constant battery of twenty cells, was placed in the solution of potassa; and another, connected with the copper of the first cell, was placed in the sulphate of copper immediately under the diaphragm which separated the two solutions. The circuit conducted very readily, and the action was very energetic. Hydrogen was given off at the platinode, or the electrode which dipped into the potassa, and oxygen at the zincode in the sulphate of copper. A small quantity of gas was also seen to rise from the surface of the diaphragm. In about ten minutes the lower surface of the membrane was found beautifully coated with metallic copper, interspersed with oxide of copper of a black colour, and hydrated oxide of copper of a light blue.

The explanation of these phenomena is obvious. In the experimental cell we have two electrolytes separated by a membrane, through both of which the current must pass to complete its circuit. The sulphate of copper is resolved into its compound anion, sulphuric acid + oxygen, and its simple cathion copper: the oxygen of the former escapes at the zincode, but the copper on its passage to the platinode is stopped at the surface of the second electrolyte, which for the present we may regard as water improved in its conducting power by potassa. The metal here finds nothing by combining with which it can complete its course, but, being forced to stop, yields up its charge to the hydrogen of the second electrolyte, which passes on to the platinode, and is evolved. The corresponding oxygen stops also at the diaphragm, giving up its charge to the anion of the sulphate of copper. The copper and the oxygen, thus meeting at the intermediate point, partly enter into combination, and form the black oxide; but from the rapidity of the action, there is not time for the whole to combine, and a portion of the copper remains in the metallic state, and a portion of gaseous oxygen escapes. The precipitation of blue hydrated oxide doubtless arose from the mixing of a small portion of the two solutions.

Experiment 19.—The experiment was repeated with a smaller electrolytic force, six of the cells of the small constant battery being substituted for the twenty cells of the large. The action was of course much less energetic, and the membrane was found thickly coated with black oxide of copper; amongst which, however, spangles of metallic copper were plainly visible. In this case there was time for the local affinity to act, and the combination of the copper and oxygen was nearly complete.

Independently of the important conclusion which these experiments confirm, namely, that in the electrolysis of a saline electrolyte, the metal travels *as a metal* towards the platinode, while all the other constituents of the salt pass, as a compound anion, to the zincode, they present the secondary action of the local affinity in striking contrast with the primary action of the current affinity in the voltaic battery: all the decompositions and recompositions of the latter, however varied and multiplied, are limited and equalized throughout the circuit, however long, by the strictest laws; while the combinations of the latter vary with every variation of time, quantity, and energy.

The experiment with sulphate of copper was repeated and varied in several ways; as by placing the solutions in a cell separated by a perpendicular, instead of a horizontal diaphragm, &c., the particulars of which I need not dwell upon; the results being always conformable to those which I have just detailed.

I next submitted other saline solutions to the same electrolytic process, the second electrolyte being in every case solution of potassa.

Experiment 20.—From nitrate of silver, metallic silver was deposited in abundance upon the membrane, mixed with oxide of silver; gas was also visibly disengaged from the diaphragm. The whole of the oxygen was not evolved at the zincode, a portion appearing to combine, by secondary action, with the oxide of silver in the nitrate, and forming a *peroxide*. It was precipitated as a brown powder, which dissolved in nitric acid with evolution of oxygen.

The experiment was varied by placing the solution of nitrate of silver in a small porous earthenware cell, which, upon examination afterwards, was found studded with minute filaments of silver, and coloured by the oxide; but this apparatus was not found to be so well adapted to the purpose as the membrane, which, from its thinness, exhibited the results of the necessarily superficial action to perfection.

Experiment 21.—Nitrate of lead afforded similar results. Metallic lead was deposited upon the bladder with oxide of lead, and, as with the silver, the oxygen was absorbed at the zincode with the precipitation of peroxide of lead.

Experiment 22.—Protosulphate of iron threw down a copious black precipitate upon the diaphragm, which, when examined with a lens, exhibited bright metallic points; but oxidation took place so rapidly, after the membrane was withdrawn from the cell, that the metallic lustre quickly disappeared.

Experiment 23.—From sulphate of palladium I obtained in a similar way metallic palladium; but it had little lustre, and did not exhibit the beautiful appearance of the copper and silver.

Experiment 24.—Protonitrate of mercury, of all the saline electrolytes which I submitted to experiment, exhibited the most striking phenomenon. Not only were metallic globules formed in abundance upon the membrane, but when the exterior cell was of glass a shower of small globules was seen to fall from the diaphragm during the whole continuance of the experiment.

Experiment 25.—I now tried sulphate of magnesia, not without hopes of finding metallic magnesium amongst the products of the experiment; but abundance of magnesia alone was precipitated upon the diaphragm. I hence conclude that the affinity of the metal for oxygen is too strong in this instance to allow of any portion escaping combination.

Combining the proofs which I have now adduced with the totally different class of evidence which I brought forward in my last communication, I think it must now be admitted that I have established the important point that, considered as electrolytes, the inorganic oxyacid salts must be regarded as compounds of metals, or of that extraordinary compound of nitrogen and four equivalents of hydrogen to which Berzelius has given the name of ammonium, and compound anions, which are exactly analogous to the simple anions, chlorine, iodine, &c. of the haloide salts; and that this evidence goes far to establish experimentally the hypothesis, originally brought forward by Davy, of the general analogy in the constitution of all salts, whether derived from oxyacids or hydroacids.

Before I proceed with the details of my experimental researches, I must beg your indulgence for a few remarks upon the subject of nomenclature, a change in which seems absolutely necessary from such a change of views; and without which it seems scarcely possible to avoid circumlocutions of the most embarassing kind, of which you will find abundant evidence in what I have already written. In speaking of salts as electrolytes, we greatly need significant expressions for the compound anions with which their metallic cathions are combined. In referring to sulphate of copper as an electrolyte, I have been obliged to designate its anion as sulphuric acid + oxygen, than which nothing can be more clumsy and, as far as the significancy of the words is concerned, erroneous. After much reflection upon the subject, it has occurred to me that the term *ion* which you have introduced to designate indifferently the two constituents of an electrolyte, and which you have further compounded into *anion* and *cathion*, to designate the elements which travel respectively to the *anode* and *cathode* of the voltaic battery, might be adopted as a general termination to denote the compounds which in the electrolysis of a salt pass to the zincode, and that they might be specifically distinguished by prefixing the name of the acid slightly modified: thus, electrolytically considered, the sulphate of copper might be called the *oxysulphion* of copper; nitrate of potassa, the *oxynitrion* of potassium. The *oxysulphion* of the former, which would travel to the zincode of the battery, would consist of $\overline{S + 4 O}$; the *oxynitrion* of the latter, of $\overline{N + 6 O}$. The *oxysulphion* of *ammonium*, or $(S + 4 O) + (N + 4 H)$, would designate the sulphate of ammonia with one equivalent of water.

The composition of words upon this principle is so extremely obvious, that I think I need not illustrate it further. I do not, of course, propose that the common designation of salts should be in all cases altered, but only when it may be necessary to speak of them in their electrical relations; and the termination *ion* will have the convenience of immediately suggesting these relations.

No one, I think, can be more alive than myself to the inconvenience of unnecessary alterations of nomenclature; they constitute an evil of no slight consideration, and have lately been, in my humble judgement, too much indulged in by chemical philosophers; but when it is sought to introduce new views and generalizations upon sufficient experimental evidence, they become absolutely necessary, and operate beneficially in assisting the mind to break through the trammels of a train of thought which is invariably attached to old expressions. Suffer me to make a moderate use of this new nomenclature in what I have further to communicate.

One of the principal objections to Davy's theory of the salts has always been the impossibility of isolating, and preserving in a free state, the compounds of acids with the additional equivalent of oxygen which it supposed; and in their electrolysis we find that the ions invariably evolve their oxygen at the zincode. It occurred to me that evidence of their isolation might be found in the beautiful experiments of M. Thenard*, which led to the discovery of oxygenated water. It will be remembered, in fact, that the first conclusion which that eminent philosopher drew from them was that the phenomena were due to such combinations of the acids with oxygen; and it was only after a long course of further investigation that he rested in the opinion that the extra equivalent of oxygen was in all cases united to the water with which they were mixed. He at the same time allowed that the combination was greatly more permanent when any acid was present. I was in hopes that I might have obtained further evidence of the fact from an apparatus which I contrived for the purpose, but the results were not conclusive, and I shall not trouble you with the details.

Experiment 26.—The apparatus consisted of a double diaphragm cell, one of the branches of which was placed in a vessel capable of holding a mixture of salt and pounded ice, by which it might be cooled to 0° Fahr. The cell was charged successively with dilute sulphuric acid, dilute phosphoric acid, and solution of sulphate of soda. The zincode was cooled by the freezing mixture, and in no instance was the oxygen evolved in proportion to the hydrogen at the platinode; and in some cases the evolution appeared to be entirely arrested. The conducting power of the circuit, however, was very much lowered by the reduction of the temperature, and was finally destroyed by the formation of ice, so that no very striking result could be obtained.

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* Annales de Chimie et de Physique, tomes viii. ix.

You will doubtless remember that in my last letter I communicated to you the anomalous and perplexing results which I obtained from the electrolysis of different mixtures of sulphuric acid and water. Every analogy led me to expect that the hydrated acid would prove an *oxysulphion of hydrogen*, and that hydrogen would be evolved at the platinode, and an equivalent of sulphuric acid with an equivalent of oxygen at the zincode. But after a great number of experiments, the results of which were consistent within certain limits, I was obliged to conclude that, for each equivalent of oxygen and hydrogen evolved, only one fourth equivalent of sulphuric acid passed to the zincode. Now it would be an extravagant hypothesis to suppose that another compound anion was evolved upon this occasion, consisting of one equivalent of sulphur and seven equivalents of oxygen, as the result of the decomposition of an electrolyte consisting of one equivalent of sulphuric acid united to four equivalents of water. The subject obviously required further investigation; and as the question appeared to me to be of first-rate importance, I bestowed much time and labour in repeating and modifying the experiments*. It would uselessly occupy your time to enter upon the details of this course of investigation; but I will briefly describe my mode of proceeding, some of the difficulties which I met with, and the means by which I attempted to obviate them.

Experiment 27.—The apparatus which I employed was of the same general nature as that which I have previously described. The gases evolved were measured and estimated in the usual manner; and the changes which took place in the relative proportions of acid and water in the two cells were approximately determined by weight, by neutralization with carbonate of soda, or by precipitation with baryta. The connecting tube (Experiment 8.) was improved by a small perpendicular tube inserted at the top of the bend, which allowed room for the expansion of the included liquid from the heat evolved, which was at times not much short of the boiling point of water. Without this precaution there was danger of some of the liquid being mechanically forced through the diaphragm, and even of rupture of the membranes.

The determinations by weight were rendered uncertain from the evaporation which took place from the surface of the liquid in the two cells at the high temperature; and it was not easy to avoid loss from the fine spray which was forcibly thrown up by the escape of the gases at the electrodes. Upon the whole, however, there was no reason to conclude that water passed to the platinode while the sulphuric acid accumulated at the zincode.

The determinations by neutralization and precipitation were much more satisfactory, and generally consistent with those which I had previously obtained. Upon a review of the whole I am quite certain that in the electrolysis of dilute sulphuric acid the quantity of acid which passes to the zincode with one equivalent of oxygen,

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* In all these experiments I was greatly indebted to the able assistance of my friend and pupil Mr. W. A. Miller, without which it would have been impossible for me to have gone through the almost numberless operations.

and for which one equivalent of hydrogen is given off at the platinode, is not more than a fourth of an equivalent, nor less than a fifth. The majority of the results, however, indicate the former proportion.

Could it be possible that a whole equivalent of acid was, in fact, carried over to the zincode, but was counteracted by that species of endosmose which I have before described, by which three fourths of an equivalent might be transported in the opposite direction to the platinode?

As this transfer is, however, more of a mechanical than of an electrolytical nature, it could not well take place without a visible rise of the liquid in the platinode cell, and none such was ever observed. It occurred to me that this question might be set at rest by multiplying the diaphragms between the electrodes. I had already succeeded, as I believed, in stopping this action by two diaphragms; it was impossible but that by adding two more some change must be produced in the amount, at least, of the endosmose, if any such really took place.

Experiment 28.—I connected the two electrode cells with a third cell by means of a second bent tube with two diaphragms, and all were charged with dilute sulphuric acid of the specific gravity 1076. The experiment was continued till seventy-one cubic inches of mixed gases had been collected in the voltameter, and lasted five hours. The acid in the three cells and two connecting tubes were then separately and carefully neutralized. The acid in the two latter and centre cell had not undergone the slightest change in quantity; but in the platinode cell it was deficient, and in the zincode cell in excess exactly eight grains.

Experiment 29.—The experiment was immediately repeated with the same acid, and two cells with one connecting tube. The same quantity of gases was collected in two hours and forty minutes, and the transfer of acid from the platinode to the zincode was found to be exactly the same without any change in the connecting tube. No doubt, therefore, can now exist that the transfer of the acid is electrolytic in its nature.

Experiment 30.—I next repeated the experiment with an amalgamated zinc, a copper, and a platinum zincode of the same dimensions. The quantity of hydrogen gas collected in each case was 23·7 cubic inches (or half an equivalent). The times were respectively forty-six minutes, fifty-four minutes, and fifty-five minutes; and the transfer of acid from the platinode was found to be in each about five grains, or one fourth equivalent for an equivalent of the gas. The zinc and copper electrodes had lost weight in proportion to the equivalent of the gas.

These last results are not without interest as regards the electromotive force of the battery. The absorption of the oxygen by the copper decreases but little the obstructions of the current, by the removal of an opposing element; but not only is the absorption of the same element effected by the zinc electrode, but an energy of one fifth, as measured by the time, added to the current.

Experiment 31.—The difference of this mere absorption of oxygen by a metal, and the additional energy of zinc in a voltaic circuit, is beautifully exemplified in the following experiment. I took ten cells of a small constant battery and charged them in the usual way, only substituting three amalgamated rods of grain tin, which had been previously weighed, for three of the zinc rods. The circuit was completed with a voltameter, and twenty-five cubic inches of mixed gases were collected in one hour; and the three rods were found to have lost respectively twenty-two grains, twenty-two grains, and twenty-one grains, or about an equivalent each for the gas. The circuit was immediately closed with the voltameter and the seven remaining zinc rods, and the same quantity of gas was collected in eight minutes. Now with regard to the mere oxidation of the metal and the removal of the oxide by the acid, everything proceeded apparently the same with the tin rods as with the zinc, and yet we find that instead of adding anything to the energy of the current, they reduced its efficiency to less than one seventh.

I cannot help remarking, by the way, that this is a result which the advocates of the *contact theory* would find it very hard to reconcile to their principles. According to their views the electromotive force of tin and copper is very little, if anything, inferior to that of zinc and copper; the resistances of all parts of the circuit are the same, and yet the addition of a few more couples of tin and copper instead of adding anything to the intensity of the current would stop it altogether.

But to return to the more immediate object of this paper. We have seen that whatever be the metal of the zincode, the quantity of acid which travels to it in the electrolysis of dilute sulphuric acid is sensibly the same, and we have yet found nothing to explain the extraordinary proportion which it bears to the gases evolved, or to make it harmonize with the results of other electrolytes.

Experiment 32.—Dilute phosphoric acid was next submitted to similar experiments. Some pure acid was prepared for the purpose; but I was at a loss for some time for a convenient and accurate method of determining the quantity of acid in any solution. This I at last satisfactorily effected by mixing it with pure oxide of lead, careful evaporation and ignition, according to the method of Professor Rose.

In the first experiment, the solution consisted of one part by weight of the glacial acid to sixteen parts of water. It conducted badly, and only 17·75 cubic inches of mixed gases (or one fourth of an equivalent) were collected in three hours and twenty-five minutes. The result was accompanied by a circumstance which I must make the subject of a future communication.

Experiment 33.—The experiment was repeated with a solution which consisted of one part glacial acid to eight of water. Twenty-four cubic inches of the gases were now collected in 2¾ hours, and the quantity of acid which had travelled from the platinode to the zincode was found to be 3·6 grs., which again is in about the proportion of one quarter of an equivalent to one equivalent of the gases. So that with phosphoric acid we have the same anomalous proportions as with the sulphuric acid.

Experiment 34.—In a postscript to my last letter I informed you that I had ascertained that, in aqueous solutions of the fixed alkalies, the oxides travel in the contrary direction to that of the acid in the dilute sulphuric acid, and that the amount thus transferred to the platinode was certainly below that of the equivalent of the gases evolved. I lost no time in endeavouring to ascertain the exact proportions; but met with some difficulty from the rapid action of the alkaline solutions upon the membranes of the connecting tube. This was at last overcome by closing the apertures with ground disks of porous earthenware tied down with pieces of calico. The mean of two experiments, in each of which 35·4 cubic inches of the mixed gases were collected, showed, by saturation with sulphuric acid, five grains of potassa transferred to the platinode, or something less than one fifth of an equivalent for an equivalent of the gases.

Experiment 35.—A solution of baryta of the specific gravity 1008·5 was found to conduct very badly, and only 7·3 cubic inches of mixed gases could be collected in five hours. The transfer of baryta to the platinode was ascertained by precipitation with sulphuric acid to be 1·53 grs., whence we may calculate that the transfer for one equivalent of the gases would be 14·84, or about one fifth equivalent: for

Mixed gases.		Mixed gases.		Baryta.		Baryta.
7·3	:	70·8	: :	1·53	:	14·84 = $\frac{76}{5}$ nearly.

Experiment 36.—A solution of strontia of the specific gravity 1007 proved to be a worse conductor even than the preceding: but the experiment was allowed to proceed for twenty-one hours, when 32·7 cubic inches of mixed gases were found to have been collected. The platinum platinode was covered with crystals of hydrate of strontia. The liquid in the zincode cell was scarcely rendered turbid by sulphuric acid, while the solution in the platinode cell afforded 14 grs. of sulphate of strontia, so that the whole of the strontia, or 7·9 grs., had passed over to the platinode. Scarcely a globule of gas was evolved from the electrodes at the time when the experiment was stopped, although the battery was still capable of evolving gas in the voltameter at the rate of about one cubic inch per minute.

Now, if we suppose that no gas was evolved after the whole of the strontia had passed over, the transfer was in the proportion of about one third equivalent for an equivalent of the gases, for

Mixed gases.		Mixed gases.		Strontia.		Strontia.
32·7	:	70·8	: :	7·9	:	17·1 = $\frac{52}{3}$ nearly,

but as it is probable that there was some excess of gas from the long continuance of the experiment, the result cannot be held to differ materially from the preceding.

Experiment 37.—I now took a solution of baryta of the specific gravity 1033 and ascertained, by precipitation with sulphuric acid, that a measure of it contained 26·9 grs. of baryta. I charged the cell with an equal measure of the same solution, and placed it in the voltaic circuit with a voltameter, with the intention of carrying on the experiment till the whole of the baryta had been transferred, as was the case with the strontia of the last experiment. The results were not examined till the expiration of forty-eight hours. The quantity of gases collected amounted to 139 cubic inches, and abundant crystals of hydrate of baryta were found around the platinode. The evolution of gas in the cell had ceased, but the battery was afterwards found to be still capable of generating gas in the voltameter at the rate of $2\frac{1}{2}$ cubic inches in ten minutes. Upon attempting to remove the cell the membranes had been so much acted upon and softened that they burst; so that it was impossible to ascertain whether the zincode cell still contained any baryta. But as it is most probable, from the duration of the experiment, that the transfer was complete, as in the case of the strontia, we have still the data for a calculation, from which it would appear that about one fifth of an equivalent of baryta was transferred for an equivalent of the mixed gases: for

Mixed gases.		Mixed gases.		Baryta.		Baryta.
139	:	70·8	: :	26·9	:	13·7

which is nearly equal to $\frac{76}{5}$ or 15.

Without ascribing to these results an accuracy which, with all the pains I could bestow, the mode of experimenting did not admit of, we may conclude, quite within the limits of possible experimental error, that in the electrolysis of aqueous solutions of acids or the fixed alkalies, the evolution of an equivalent of oxygen at the zincode is accompanied in the first instance by an accumulation of acid, which cannot exceed one fourth of an equivalent, or fall short of one fifth; and the evolution of hydrogen at the platinode in the second case, by an accumulation of alkali to an amount within the same limits.

Now with regard to the alkaline experiments it is, I conceive, still more impossible to believe that the cathion which travelled to the platinode was an association of an equivalent of potassium, or other metal, with three equivalents of hydrogen (the fourth being due to the reaction of the metal upon the water), than to believe that, in the sulphuric acid experiments, the anion which went to the zincode was a compound of one equivalent of sulphur and seven equivalents of oxygen. What must we then conclude?

Shall we suppose that the electrodes of the battery are endued with an attractive power for different kinds of matter, in virtue of which free acids pass to the zincode and free alkalies to the platinode? Shall we further imagine that the proper electrolytic force of the current, with regard to water, is assisted by this adventitious force, so that water which contains either free acid or alkali is a much more efficient conductor, and is more abundantly decomposed than pure water?

I will not dwell upon other objections to this hypothesis, but I must own my utter unwillingness to return to a notion which I think your "Experimental Researches" have so completely subverted; and it would require much stronger considerations than the pressure of the present difficulty to make me abandon your definition of the electric current as "an axis of power having contrary forces, exactly equal in amount, in contrary directions*." I am, moreover, not without hopes that you will consider

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* Experimental Researches, § 517.

the results of my next experiment as furnishing a key to the mystery which has occasioned me so much perplexity and labour.

Experiment 38.—I was naturally anxious to complete my electrical examination of the sulphates by the electrolysis of the *bi-salts* of this class, and for this purpose I made a strong solution of pure crystallized bi-sulphate of potassa; and carefully ascertained its neutralizing power, by the alkalimeter, and also, by evaporation and ignition with carbonate of ammonia, the quantity of *neutral* sulphate which a certain measure of it contained. I then exposed an equal measure of the solution to the voltaic current in each of the arms of the double diaphragm cell till 70·8 cubic inches of the mixed gas had been collected. Half of the solutions from the zincode and platinode were then separately neutralized, and half evaporated and ignited.

Upon a calculation for the whole quantity, the zincode solution appeared to have gained eighteen grains of acid, and the platinode to have lost nineteen grains, while the zincode had lost fifteen grains of neutral sulphate, which are equivalent to 8·2 grs. of potassa, and the platinode had gained something less.

Experiment 39.—The experiment, the results of which appear to me to be extremely important, was immediately repeated, and the losses and gains of the zincode and platinode solutions corresponded still more closely than before. With regard to the acid, the gain of the zincode was eighteen grains, the loss of the platinode nineteen grains. With regard to the potassa, the gain of the platinode was 9·9 grs., and the loss of the zincode exactly equal.

Hence it appears that the law of the electrolysis of the *bi-salt* is very different from that of the *neutral* salt: the solution conducted very well, but as estimated by the potassa transferred to the platinode, not more than one fifth of an equivalent was decomposed for an equivalent of hydrogen evolved at the same electrode. This was accompanied by the transfer of half an equivalent of acid to the zincode, where a whole equivalent of oxygen was also given off.

I think that we cannot hesitate to admit that, in this case, the current divided itself between two electrolytes, and that a part was conducted by the neutral sulphate of potassa, and a larger part by the sulphuric acid and water, after the manner of the solutions upon which we have dwelt so long. It is a well known fact that the voltaic current will divide itself between two or more metallic conductors in inverse proportion to the resistance which each may offer to its course; and that it does not in such cases choose alone the path of least resistance; and, in a former communication* to you, I pointed out some curious instances of *diverted currents* in which liquid electrolytes were concerned. I am not aware that such a division of a current between two electrolytes in the same solution has ever before been pointed out, but analogy would lead one to expect it.

With this new view let us now revert first to the experiments with the dilute sulphuric acid. If we regard this acid as a mixture of the two electrolytes, *oxisulphion*

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* Philosophical Transactions, for 1837, p. 119.

of hydrogen $H + (S + 4\,O)$ and water $(H + O)$, we may derive an explanation of the phenomena much more consistent with the laws of electrolysis which you have established than any which has yet presented itself. In this case the current divides itself between the two so as to effect the decomposition of three equivalents of water and one equivalent of the *oxisulphion*, and thus four equivalents of hydrogen will be evolved at the platinode, and four equivalents of oxygen with one equivalent of sulphuric acid at the zincode.

The explanation of the alkaline decompositions is no less easy. The solution of potassa, for instance, is a mixture of the two electrolytes, oxide of potassium $(P + O)$ and water $(H + O)$: the current divides itself between the two, and electrolyses one equivalent of the former, and three equivalents of the latter. Four equivalents of oxygen make their appearance at the zincode, one derived from the oxide of potassium and three from the water; and four equivalents of hydrogen at the platinode, one of which is due to the secondary action of the metal upon the water.

In the second place, let us resume the consideration of the experiment with bisulphate of potassa. We have already seen reason to conclude that the solution of this salt acts as a mere mixture of neutral sulphate and sulphuric acid in water; and that the current is conducted in a small part by the decomposition of the salt, and still more abundantly by the dilute acid. We must now consider the solution as containing three electrolytes, namely *oxisulphion of potassium* $P + (S + 4\,O)$, *oxisulphion of hydrogen* $H + (S + 4\,O)$, and water $(H + O)$, and the results of the electrolysis agree very well with the supposition that the current divides itself between the three, so as to effect the decomposition of one equivalent of *oxisulphion of potassium*, one equivalent of *oxisulphion of hydrogen*, and two equivalents of water.

The two following Tables will exhibit the results of the actual experiment, and those of an equivalent calculation founded on the hypothesis; from a comparison of which it will appear that, considering the numerous sources of inaccuracy in the experiments, the agreement is very close: taking, indeed, the different quantities of sulphuric acid as the more certain measure of the effects it is almost perfect.

TABLE I. Experimental Results.

Before the electrolysis the solution contained

Neutral salt.		Acid.		Alkali.	Free acid.
104·2	=	47·3	+	57	44
Zincode after Electrolysis.					
86·0	=	39·0	+	47	64
(−18·2)		(−8·3)		(−10)	(+20)
Platinode after Electrolysis.					
122·0	=	55	+	67	26
(+18·2)		(+8·3)		(+10)	(−18)

TABLE II. Calculated Results in Equivalents.

Before the electrolysis the solution contained

Neutral salt.		Acid.		Alkali.	Free acid.
96·8	=	44	+	52	44
		Zincode after Electrolysis.			
72·6	=	33	+	39·6	66
(−24·2)		(−11·0)		(−13·2)	(+11×2)
		Platinode after Electrolysis.			
121·0	=	55·0	+	66·0	22
(+24·2)		(+11·0)		(+13·2)	(−11×2)

According to this view, the electrolysis of an equivalent of bisulphate of potassa in water would yield at the zincode four equivalents of oxygen, one of which would be derived from one equivalent of *oxisulphion of hydrogen*, a second from one equivalent of *oxisulphion of potassium*, and two from two equivalents of water, together with two equivalents of sulphuric acid which would remain in solution: and at the platinode, four equivalents of hydrogen, one from the *oxisulphion of hydrogen*, a second from the secondary action of an equivalent of potassium upon the water of the solution, and two from the electrolysed water, together with one equivalent of potassa in solution.

I must again guard myself by stating, that I do not think the accuracy of the experiments sufficient to determine whether the proportions of the electrolytes decomposed are, as I have just represented them, three to one, or four to one; or whether the proportions with regard to water are always the same with respect to them all; but if so, and the results justify the suspicion, the electrolyte, water, must exercise a limiting power upon other electrolytes, which is well worthy of further careful investigation. The reaction also of other electrolytes upon water, by which its conducting power is so greatly increased, still remains involved in obscurity.

The electrolysis of sulphate of copper, under certain circumstances, is attended by a remarkable effect, which I think may be explained by the principle just laid down. You will remember that in my account of the construction of the *constant battery*[*] I attributed the precipitation of the copper from the sulphate to "the deoxidating power of the nascent hydrogen;" but from the first I have been generally struck with the beautiful crystalline arrangement and close compact structure of the metallic deposit. This is so remarkable, that in the first small sheet of copper which I stripped from a platinum electrode, and which is now in my possession, I noticed that the scratches of the file, which the latter bore, were perfectly moulded upon it. This is unlike what one would have expected, *à priori*, from the precipitation of a metal, by a

[*] Philosophical Transactions, 1836, p. 117.

gas adhering to the surface of the electrode, and is much more consistent with, what we now know to be the fact, the immediate deposit of the metallic cathion upon the platinode without the intervention of the gas. I had also remarked, at times, without being able to account for it, that the texture of the copper was spongy and little coherent.

The beautiful application of this observation by Professor Jacobi and Mr. Spencer to the formation of fac-similes of medals and other *volta-types*, as I have proposed to call them, has made us better acquainted with the minutest details of this kind of precipitation; and every one who has attended much to the process, must have observed that, in conducting it in the usual way, after the same solution has been a long time in use, the deposit of compact copper became mixed with copper in a loose, pulverulent state, which can be brushed off the mould with the fingers, and greatly interfered with the beauty of the result. This arises from the accumulation of acid in the solution from the decomposed sulphate; and I have no doubt that *oxisulphion of hydrogen* being thus formed, the current is divided between it and the *oxisulphion of copper*; and that the pulverulent copper is owing to the secondary action of the hydrogen disengaged from the former upon the solution.

Experiment 40.—I have from the first prevented this injurious effect in Mr. Spencer's process, by making the precipitation in a separate cell, containing the sulphate of copper, connected with two or three cells of the constant battery by a copper zincode; by this arrangement the copper was dissolved at the zincode as fast as it was deposited at the platinode, and the accumulation of acid prevented.

I shall now only trouble you with a brief account of two or three more experiments, the results of which throw some additional light upon the electrolysis of secondary compounds.

Experiment 41.—I was anxious to ascertain in what manner the *carbonates* would conduct themselves as electrolytes, and particularly the relation which they would exhibit to the *oxalates*. For this purpose the carbonates of potassa, soda, and ammonia were subjected to the voltaic action in the double diaphragm tube, the zincode cell of which was sometimes connected with a Liebig's tube, for the purpose of absorbing the carbonic acid; and carbonic acid and oxygen were found to be given off in equivalent proportions to the alkali and hydrogen at the platinode; proving these salts to be *oxicarbions* of potassium, sodium, and ammonium respectively.

Experiment 42.—Oxalate of ammonia, treated in the same way, yielded nothing at the zincode but carbonic acid, and ammonia with hydrogen at the platinode. When the constitution of the oxalic acid is remembered, this result will be very intelligible; for

$$\overset{\text{Oxalic acid.}}{(2\,C + 3\,O)} + O = \overset{\text{Carbonic acid.}}{2\,(C + 2\,O)},$$

the one equivalent of oxygen being quite sufficient to convert the one equivalent of oxalic acid into two equivalents of carbonic acid.

Nevertheless the oxalate must be looked upon as an *oxalion of ammonium,*

$$(C + 4\,O) + (N + 4\,H)$$

and the production of the carbonic acid as a secondary effect.

I am inclined to believe that the discovery of a mode of electrolyzing any of the numerous combinations of hydrocarbon, so as to isolate that principle or carbon, would tend more to advance our knowledge of organic compounds than any other single step which could be taken; and I was not without hopes that the *sulpho-vinates* might afford some indications which might lead to such a process.

Experiment 43.—I therefore subjected some pure sulpho-vinate of potassa, for which I was indebted to the kindness of Mr. HENNEL, to the action of the voltaic current in the double diaphragm cell. It proved to be a very good conductor, and the results were not ambiguous. Sulphovinic acid and oxygen were collected at the zincode, and potassa and hydrogen, all in equivalent proportions, clearly establishing this salt as a *sulphovinion of potassium.*

Permit me, now, before I close this letter, to make a few observations upon a subject which strikes me as closely connected with the compound electrolytes upon which I have dwelt at such length; I mean the origin of the currents in BECQUEREL's *battery*. I never could bring myself to believe that the mere combination of the acid and alkali could give rise to such a current, and have always thought that you have abundantly proved its impossibility. And yet there is now a mode of viewing such a combination, which I think may explain the phenomena.

Experiment 44.—I have carefully repeated and varied the experiments, for the purpose of possessing myself accurately of the facts. I chiefly made use of solutions of nitric acid and potassa placed on either side of a diaphragm of bladder in a divided glass cell, which could be firmly bound together with brass clamps. Platinum electrodes were placed on either side of the diaphragm.

I satisfied myself not only of the usual phenomena with the galvanometer, but that oxygen was evolved on the potassa side, and hydrogen on the nitric acid side. The former I had no difficulty in collecting in an inverted closed tube; the latter was recognised by its secondary action upon the nitric acid. Nitrate of potassa was of course formed at the junction of the acid and alkali. Now let us recollect what nitrate of potassa is in its electrical relations: it is an *oxinitrion of potassium* $(N + 6\,O) + P$. Aqueo-nitric acid is also an *oxinitrion of hydrogen* $(N + 6\,O) + H$; and potassa is oxide of potassium $(P + O)$. In their local action upon each other, the acid and the alkali are both decomposed; the oxinitrion of the former combines with the metal of the latter, and water is formed by the union of the hydrogen and oxygen. This water there is no difficulty in regarding as a separate and secondary product, in as much as the salt is incapable of combining chemically with it.

When a circuit, however, is formed with proper conductors, the compositions and recompositions take place through a series of connected particles, as in the manner of all other electrolytic conduction: and the oxygen and hydrogen instead of combining together, as in the local action, are respectively evolved at the zincode and platinode. The following diagrams may perhaps assist in explaining my notion of the origin and connection of the current.

$$\overgroup{OP}\;\overgroup{OP}\;\overgroup{OP}\;\overset{A}{\underset{B}{|}}\;(N+\overgroup{6\,O)\,H}\;(N+\overgroup{6\,O)\,H}\;(N+\overgroup{6\,O)\,H}$$

Let $\overgroup{OP}$ and $(N+\overgroup{6\,O)\,H}$ represent the two electrolytes on the opposite sides of the diaphragm A B before action; after action has commenced they may be represented thus:

$$O\,\overgroup{P\,O}\,\overgroup{P\,O}\,\overgroup{P\,\overset{A}{\underset{B}{|}}\,(N}+6\,O)\,\overgroup{H\,(N}+6\,O)\,\overgroup{H\,(N}+6\,O)\,H$$

May I not ask, in conclusion, whether such a current does not again defy any explanation upon the contact theory?

Believe me, dear FARADAY,

Very faithfully yours,

J. F. DANIELL.

King's College,
29th April, 1840.