VII. *On the Electrolysis of Secondary Compounds. In a Letter 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., Prof. Chem. in King's College, London.*

Received May 15,—Read June 13, 1839.

MY DEAR FARADAY,

I HAVE no doubt that you will agree with me in thinking that the decomposition of secondary compounds by the voltaic current, particularly in connexion with water, has not yet received all the attention which it deserves, and that the subject is worthy of further experimental research.

When water is present in an electrolyte, you have yourself remarked* that it is probable that it is always resolved into its first principles; and, on the other hand, the early experiments of Sir H. DAVY prove that when saline substances are present in water, even in the minutest quantities, they are also separated into their elements, or into their proximate principles. Whether these simultaneous decompositions bear any relation to each other, has never, that I am aware of, been made the object of inquiry.

Your discovery of definite electro-chemical action has rendered it of great importance to ascertain, in the case of the decomposition of a saline solution, what proportion of the current may be carried by the oxygen and hydrogen of the water, and what by the acid and alkali, or non-metallic and metallic element, of the salt; and whether there be any definite connexion between the two electrolytes so decomposed. This question was the origin of the following investigation, the results of which have disclosed views of the nature of compound electrolytes and of secondary chemical combinations, which I trust may not be found unworthy of the attention of the Royal Society.

The power which I employed in the following experiments was that of a small constant battery of thirty cells six inches in height, with tubes of earthenware charged in the manner which I have formerly described; and I cannot but remark that without such an instrument the investigation could not have been carried on. The battery was in action almost daily for more than two months, generally from five to six hours per day, and the copper cylinders have thereby become considerably thicker and heavier. Neither the expense nor the uncertain action of batteries of the old construction would have admitted of such an use.

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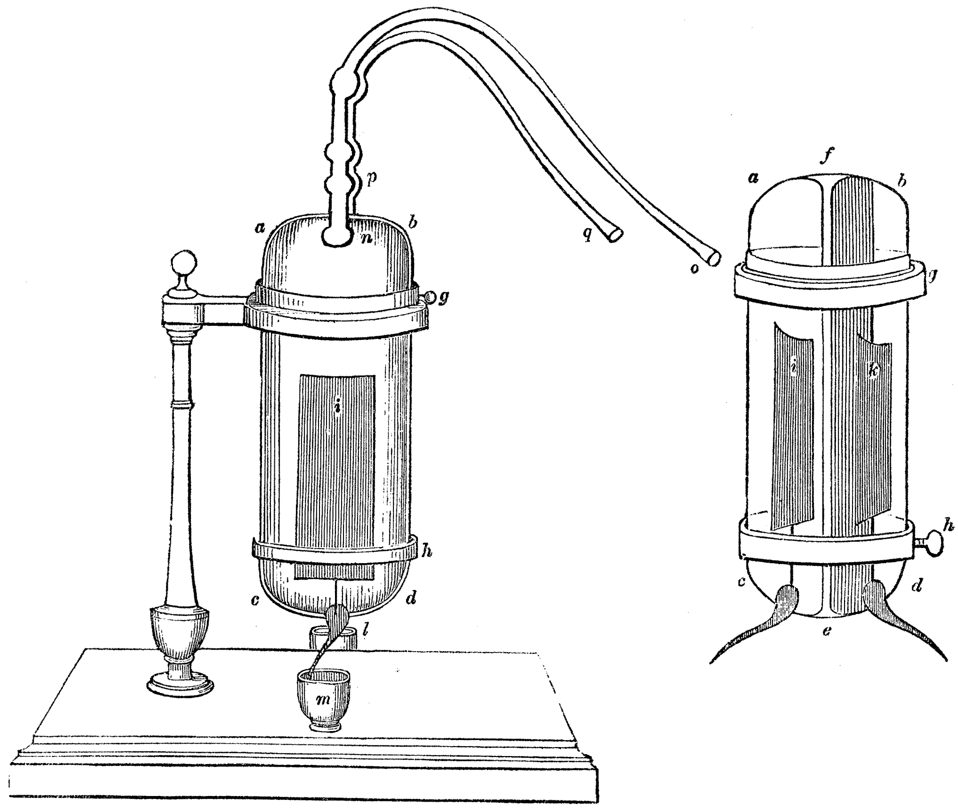
* Experimental Researches in Electricity, § 671.

The experimental cell which I first employed consisted of a stout glass cylinder, capable of holding about fourteen cubic inches of liquid, which was originally closed at both extremities. It was cut longitudinally into two equal parts, for the purpose of inserting between the halves a thin plate of fine porous earthenware, which, when the whole was again clamped together by brass rings with screws, divided it into two compartments. The wire of a platinum electrode, 2¾ inches in length and one inch in width, passed through the bottom of each compartment; and to the top of each was ground a bent glass tube for the purpose of collecting the gases evolved during the experiments. The following cut represents a front and side view of the apparatus.



a b c d is the glass cylinder; *e f* the porous diaphragm; *g h* the brass rings and screws by which the two halves are clamped together; *i* and *k* are the two electrodes; *l* and *m* the mercury cups by which the connexions are made with the battery; *n o* and *p q* are the bent tubes by which the gaseous products are collected.

In a preliminary trial one of the compartments was filled with distilled water, and remained for twenty-four hours without penetrating to the other in any appreciable quantity.

A mixture of sulphuric acid and water was prepared beforehand for the purpose of ascertaining in the usual way, by the alkalimeter tube, the amount of any alkaline matter which it might be employed to neutralize; and a similar solution of carbonate of soda for measuring acids. In calculating the results of the experiments, 70·8 cubic inches of mixed hydrogen and oxygen gases have been taken as equivalent to nine grains of water, or one equivalent upon the hydrogen scale expressed in grain weights; and to facilitate computation and comparison, as well as to obtain quantities which might be certainly measured, the experiments were generally continued till the quantities of gases collected indicated a half or a whole equivalent.

Experiment 1.—The cell was charged with a solution of sulphate of soda of the specific gravity 1052, so as to cover the electrodes and to fill about half its capacity. When connexion was made with the battery it was found to conduct well; and the decomposition was allowed to proceed till twenty cubic inches of hydrogen had been collected from the platinode, and nine cubic inches of oxygen from the zincode.

The platinode solution was drawn off carefully with a glass syphon, and found to be strongly alkaline, and to contain by the alkalimeter 12 grains of free soda. The zincode solution was very acid, and neutralized carbonate of soda equivalent to 15·1 grains of sulphuric acid.

The results, therefore, of even this first experiment evidently indicate that the decomposition of an equivalent of water was accompanied by the decomposition of an exact equivalent of sulphate of soda, for the differences are but of inconsiderable amount. I shall not dwell upon the want of exact correspondence between the oxygen and hydrogen, for these are well understood; but taking the amount of the mixed gases as corrected for pressure and temperature at 28·3 cubic inches, we have the following proportions.

Cubic in.		Cubic in.		Equiv. of soda.		Soda.
70·8	:	28·3	: :	32	:	12·8
				Equiv. of sulph. acid.		Sulph. acid.
70·8	:	28·3	: :	40	:	16·1

The experimental results of 12 soda and 15·1 sulphuric acid are not more below the calculated results than might have been expected from the mode of experimenting. It must also be observed, that the level of the solution in the two divisions of the cell altered very much during the experiment; and at its termination the liquid stood 1½ inch higher at the platinode side than at the zincode.

These exact equivalent results are by themselves very remarkable; but I was now anxious to ascertain whether the power of the current were equally divided between, what had hitherto been considered to be, the true equivalent electrolytes.

Experiment 2.—The last experiment was repeated with the same solution of sulphate of soda; but a voltameter, whose electrodes were of the same dimensions as those of the experimental cell, charged with the standard mixture of sulphuric acid and water, was included in the circuit. The experiment was carried on till 70·8 cubic inches of mixed gases had been collected from the voltameter, when it was found that the hydrogen from the platinode of the experimental cell was 47·5 cubic inches, and the oxygen from the zincode 20·25 cubic inches. The former is almost exactly equal to the hydrogen indicated by the voltameter, while the latter is a little short of the equivalent proportion of oxygen. There can, however, be no doubt that the quantities of mixed gases from the saline solution and from the dilute sulphuric acid were equal. Free acid and alkali were found at the zincode and platinode respectively, as in the first experiment, but owing to an accident were not neutralized.

Now if we regard, in the usual way, the convection of the current as effected in the voltameter by the transfer of the oxygen and hydrogen alone, we appear at first to be led to this extraordinary conclusion, namely, that the same current, which is just sufficient to separate an equivalent of oxygen from an equivalent of hydrogen in one vessel, will at the same time separate an equivalent of oxygen from hydrogen, and an equivalent of sulphuric acid from an equivalent of soda, in another vessel. The clearing up of such a result must obviously be of the first importance.

As secondary objects of interest in this experiment, it may be observed, that the temperature of the liquid in the experimental cell rose to 130° Fahr., while that of the acid in the voltameter did not exceed 67°, the quantity of the former considerably exceeding that of the latter; and that the transfer of liquid from the zincode to the platinode occurred as before, so that at the end of the experiment the level of the latter was considerably above that of the former.

The second experiment was repeated twice, and both times the disengaged acid and alkali were neutralized, and found to be in equivalent proportion to the oxygen and hydrogen given off by the electrodes of the experimental cell; which again were together equal to the mixed gases simultaneously given off by the attached voltameter. When the process was continued too long, the proportions of acid and alkali fell short of that of the gases, and that in proportion to the time of its continuance. This was doubtless owing to the gradual mixing of the liquids on the two sides of the diaphragm, and the consequent recombination of the acid and alkali. In every case, transfer of the liquid took place from the zincode to the platinode, and the temperature of the experimental cell rose far above that of the voltameter.

Experiment 3.—The experimental cell was charged with sulphate of potassa of the specific gravity 1069; and a similar cell with dilute sulphuric acid of the specific gravity 1150, coloured on the zincode side with indigo. Both were included in the circuit. After forty minutes action, the saline solution had risen on the platinode side one-fourth of an inch, and fallen to the same amount on the zincode side, while no transfer of liquid had taken place in the acid cell, nor had any colouring matter passed from the zincode side of the diaphragm to the platinode. The indigo, however, had entirely lost its blue colour and become yellow. The amount of mixed gases from both cells was nearly equal; but the oxygen from the acid fell a little short of that from the salt, in consequence, probably, of its absorption by the indigo. The acid disengaged at the zincode and the alkali at the platinode of the saline solution, were also found to be in equivalent proportions to each other and to the gases.

Experiment 4.—A solution of nitrate of potassa of the specific gravity 1117 was substituted for the solution of sulphate of potassa in the last experiment; five cubic inches of oxygen were given off by the zincode, and 4·3 cubic inches of hydrogen only from the platinode. Upon opening the apparatus, a strong smell of ammonia was evolved from the platinode side; evidently indicating a secondary action of the hydrogen upon the nitric acid of the nitre, and accounting for its deficiency. After driving off the ammonia by heat the solution was still alkaline, and by neutralization indicated 13·5 grains of potassa. The neutralization of the acid on the zincode side indicated 17 grains of pure nitric acid. These numbers do not differ much from equivalent proportions, which, upon the assumption that the determination of the acid was correct, would be 17 nitric acid, and 15·1 potassa; or, preferring the determination of the alkali, would be 15 nitric acid, and 13·5 potassa. The quantity of water simultaneously decomposed we can only, in this instance, estimate from the quantity of oxygen collected, which, as we have seen, generally falls below its due proportion; but still it comes near enough to the equivalent proportion to assure us that this would have been the correct determination for

Cubic inches.		Equivalent of nitric acid.		Cubic inches.		Nitric acid.
70·8	:	54	: :	15·0	:	14·2

In this experiment, less of the solution was carried from the zincode to the platinode, and the difference of the level did not exceed $\frac{3}{16}$ths of an inch.

Experiment 5.—The experiment was repeated with the substitution of a solution of phosphate of soda of the specific gravity 1057 for the nitrate of potassa, and the results left no doubt that the simultaneous decompositions of the salt and the water were in equivalent proportions as before. In this experiment, a larger quantity of the solution was carried from the zincode to the platinode than in any of the preceding instances, and the difference of the level on the two sides of the diaphragm amounted to two inches.

Before I proceed with the principal object of this inquiry, I will make one or two remarks upon this extraordinary transfer of matter from one electrode to the other without the decomposition of the transported compound. It was first observed by Mr. PORRET*, who found it to take place in a glass cell divided into two by a diaphragm of bladder. Into each compartment, filled with water, he plunged a platinum plate and connected the two with the two extremities of a voltaic battery of eighty couples, and nearly the whole of the liquid in the positive cell was carried into the negative cell. It was afterwards found that this phenomenon did not take place when the conducting power of the water was improved by the addition of sulphuric acid.

M. BECQUEREL has also shown† that when finely-divided clay is placed about the water at the zincode in a tube separated from the platinode by a porous diaphragm, the particles of clay are carried forward by the current which is established. This transfer he has also observed to take place only when the water conducts badly.

I charged the experimental cell with the porous diaphragm with distilled water, and found, with the battery of thirty cells, that a few bubbles of gas formed upon the

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* Annals of Philosophy, July 1816.

† Traité de l'Electricité, tom. iii. p. 102. par M. BECQUEREL.

electrodes, but that none was disengaged: in forty minutes, however, the liquid in the platinode cell stood half an inch higher than that in the zincode. This experiment was repeated, a little fresh precipitated alumina having been diffused in the water on the zincode side: a portion of this finely-divided solid matter evidently passed with the water which was transferred to the platinode side.

When the water was saturated with boracic acid, its conducting power was a little improved; but still no measurable quantity of gas was given off, and in forty minutes the difference of level in the two compartments of the cell was $\frac{3}{16}$ths of an inch. When the cell was charged with a mixture of eight parts water and one part sulphuric acid, no change of level took place on the two sides.

Notwithstanding the good conducting power, however, of the saline solutions, we have seen that this passage of liquid from the zincode to the platinode occurs with them even to a greater extent than with pure water, and the different species of salts seem to be acted upon in different degrees.

To ascertain whether, during this process of convection, any separation took place of the salt from its solvent, I took the specific gravity of the solutions both before and after the process, and found the differences so trifling as evidently not to arise from this cause. Neither does this large transfer of matter, which is always in the same direction, seem to interfere with the definite electrolytic effect of the current by which it is produced. This will be shown still more strikingly from the subsequent experiments. Whatever may be its proximate cause, the phenomenon appears to be analogous to the transfer of good conducting matter which takes place from the zincode to the platinode during the disruptive discharge of the battery in air, which I referred to in my last communication*, and in which I pointed out to you that the platinum of the zincode was carried forward and deposited upon the charcoal of the platinode. I am also disposed to think that it is quite distinct from the process which M. DUTROCHET has named *endosmose* and *exosmose*, which may be satisfactorily explained by the force of heterogeneous adhesion, without reference to electrical currents.

I have already stated that the products of electrolyzation cannot be kept long separate in the cell which I have described, on account of the ultimate mixture of the liquids on the platinode side of the diaphragm; I was, therefore, led to construct an apparatus which answers this purpose much more perfectly, and which, for distinction, I shall call the double diaphragm cell. It consists of two cells formed of two glass cylinders, with collars at their lower ends, fitted by grinding to a stout glass tube bent into the form of the letter U, and firmly fixed on a wooden foot. The ends of this piece project a little into the interior of the two cylinders, the upper extremities of which are furnished with bent tubes for the collection of gases. A stout piece of platinum wire is ground into the upper part of each cell, to which an electrode of platinum or any other metal can be screwed on the inside, as occasion may require: the wires pass down upon the outside, and terminate in two mercury cups, by

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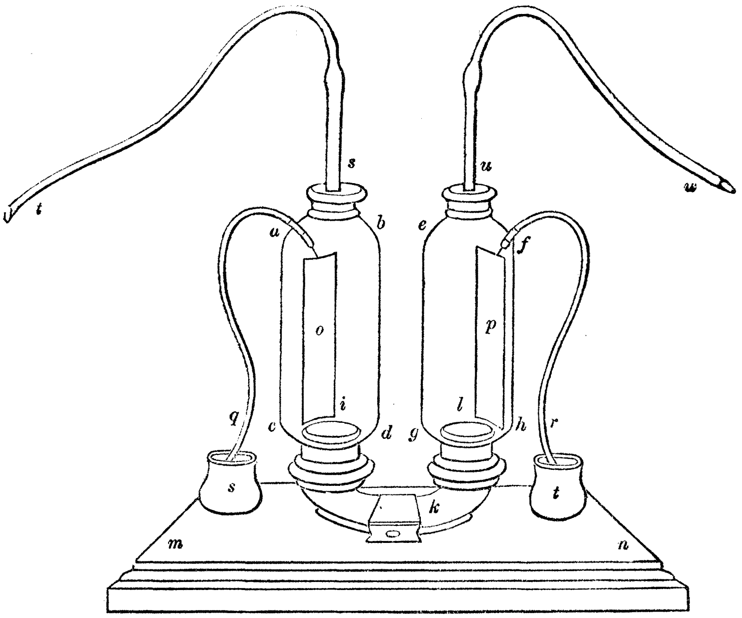
* Present Volume, p. 92, *et seq.*

which connexion can be made, at pleasure, with the battery. Each cell will hold about seven cubic inches of liquid, and the connecting tube two cubic inches. When the cell is charged, the connecting tube is filled with the liquid, and a piece of fine bladder tied over each end, so as perfectly to exclude the air. The bladders are firmly confined to their places by means of circular grooves ground round the ends of the glass tube. The cylinders are then carefully fitted to their places, and filled with the proper quantities of the solutions to be acted upon, and after the operation their contents are easily decanted, by means of a small glass syphon.

The apparatus is delineated in the following cut.



a b c d and *e f g h* represent the two glass cells; *i k l* is the bent glass tube fixed in the wooden stand *m n*; *o* and *p* are the electrodes connected with the mercury cups, *s* and *t*, by the wires *a q* and *f r*; *s t* and *u w* are the bent tubes for the collection of the gases evolved.

The current when transmitted by this double cell was, of course, much more retarded than by the single cell, on account of the greater distance of the electrodes, but it answered its intended purpose of stopping the transfer of the liquid even in the case of saline solutions, and there was still conducting power enough to render it perfectly effective. The bladders, however, of the connecting tube generally became a little cupped; indicating a pressure from without, owing to a transfer of a small portion of the liquid within.

Experiment 6.—The two cells were charged each with $4\frac{1}{2}$ cubic inches of a saturated solution of sulphate of soda, and the connecting tube was also filled with the same, and in $2\frac{1}{4}$ hours the hydrogen evolved from the platinode was twenty-four cubic inches, and the oxygen from the zincode ten cubic inches, making a total of the mixed gases of thirty-four cubic inches; or, making allowance for the deficiency of oxygen, about half an equivalent. After the experiment, the quantities of liquid in the two cells were found unchanged. The zincode solution indicated by saturation the existence of 19·2 grains of free sulphuric acid, and the platinode solution 13·5 grains of free soda, to which must be added two grains of soda in the connecting tube; making a total of 15·5 grains of soda. These numbers are almost identical with the half equivalents of sulphuric acid and soda.

This and similar experiments were frequently repeated with perfectly consistent results; but it will be unnecessary to occupy your time with their details, as I consider that I have already adduced sufficient evidence to prove, that, in the electrolysis of a solution of a neutral salt in water, a current which is just sufficient to separate single equivalents of oxygen and hydrogen from a mixture of sulphuric acid and water will separate single equivalents of oxygen and hydrogen from the saline solution, while single equivalents of acid and alkali will make their appearance at the same time at the respective electrodes.

Experiment 7.—It now seemed to me desirable to ascertain whether in the electrolysis of the dilute sulphuric acid any transfer of the acid took place; and for this purpose, after having taken the specific gravity of the mixture, each cell was charged with five cubic inches of the acid, and the connecting tube also filled with it. In little more than an hour's time after connexion with the battery, the oxygen collected from the zincode amounted to 23·6 cubic inches, and the hydrogen at the platinode to 47·5 cubic inches, or the two gases together to 71·1 cubic inches. The specific gravity of the acid before the experiment was 1126·6. After the experiment, the bulk of the acid both at the zincode and platinode was found unchanged; but, at the former, the specific gravity had increased to 1130·3, and at the latter it had decreased to 1120·3. In a repetition of this experiment, the cells were charged with four cubic inches instead of five cubic inches of acid of the specific gravity 1128·0, and after the collection of the same quantity of the mixed gases, the specific gravity of the acid at the zincode was found increased to 1141·0, and that of the platinode decreased to 1123·0.

From these experiments we learn, that during the electrolysis of an equivalent of water, a portion of acid passed from the platinode to the zincode, and possibly of water from the zincode to the platinode; and, from the greater increase of specific gravity in the smaller quantity of the mixture than in the larger, that the quantities were nearly equal in the two experiments.

But this method did not appear to me capable of determining the point with that precision which its importance rendered desirable; I therefore endeavoured to ascertain the quantity of acid transferred by actually weighing the cells before and after the process.

Experiment 8.—I made use of an apparatus in which the connecting tube covered with its two diaphragms was placed at the top of the two cells, its ends dipping below the surface of the liquid which they contained. The quantity of water decomposed was ascertained by a voltameter included in the circuit. The mixed gases collected amounted to eighteen cubic inches. The weights of the different parts of the apparatus charged with the dilute acid before and after the experiment were as follows:

	Before experiment. grs.	After experiment. grs.	gr.
Connecting tube . . .	539·2	537·3	1·9 loss.
Platinode cell	2687·8	2685·2	2·6 loss.
Zincode cell.	2631·5	2634·0	2·5 gain.
	5858·5	5856·5	
Total loss		2	
	5858·5	5858·5	

Now if we multiply the amount of the gases by four, the product will be seventy-two, or nearly an equivalent of water decomposed. The total loss, two grains multiplied by four, will be eight grains, which is sufficiently near the equivalent weight of water to lead to the conclusion that the difference arises from errors in experiment: and 2·5 grains, the quantity of acid transferred, multiplied by four, will give ten grains as the amount of sulphuric acid transferred during the electrolyses of one equivalent of water.

This experiment was several times repeated, and the result was always a small gain of weight in the zincode cell, and a loss in the platinode; but I found that I could not rely upon this method of operating for the accurate determination of quantities which it was my object to obtain.

Experiment 9.—I therefore returned to the double diaphragm cell, which I charged with dilute sulphuric acid of different degrees of strength, and having ascertained the quantity of crystallized carbonate of soda which each mixture would neutralize before the experiment, I measured the neutralizing power of each cell after it had been exposed to the battery current. The process was continued in most cases till 70·8 cubic inches of the mixed gases had been collected; and, for the sake of comparison, in the following table, the results have been all brought up to one equivalent by calculation.

Table showing the saturating power of dilute sulphuric acid at the two electrodes for one equivalent of water decomposed.

	1 Acid. 8 Water.	1 Acid. 16 Water.	1 Acid. 32 Water.	1 Acid. 64 Water.	1 Acid. 128 Water.	1 Acid. 8 Water.
Platinode ..	−24	−29	−32	−37	−39	−35
Zincode	+20	+35	+31	+37	+36·5	+36

Now, if we reject the results of the first experiment (for which, however, I have been unable to discover any reason except their inconsistency with the others,) all the rest agree very closely together, notwithstanding the great differences in the mixtures of acid and water from which they were obtained. The mean result also accords very well with the determination at which we had arrived, in Experiment 8, of the transfer of ten grains of sulphuric acid from the platinode to the zincode for every nine grains of water decomposed for

Equivalent of crystallized carbonate of soda.		Equivalent of sulphuric acid.		Carbonate of soda.		Sulphuric acid.
144	:	40	: :	36	:	10

The experiments, however, I conceive, are not sufficient to determine whether the differences of neutralizing power are owing solely to the transfer of acid from the platinode to the zincode, or whether they arise partly from such a transfer, and partly from a simultaneous passage of water from the zincode to the platinode. I have been unable as yet to contrive any experiment to determine this point, which is one of considerable interest.

Experiment 10.—Wishing now to vary the conditions of the last experiment, and at the same time to ascertain whether the same transfer of acid takes place in the active cells of the battery, where the oxygen of the decomposed water is taken up by zinc instead of being given off from a platinum surface, I substituted an amalgamated zinc plate for the platinum in the zincode cell. Its weight before the experiment was 442·5 grains. Each cell was charged with 1123 grains of dilute acid, containing, by calculation from its neutralizing power, 158·8 grains of anhydrous acid. The action of the battery was continued till 23·5 cubic inches of hydrogen had been collected from the platinode, indicating the decomposition of half an equivalent of water. After the experiment, the zinc electrode weighed 426·5 grains, the deficiency being sixteen grains, or half an equivalent of zinc.

The saturation of the liquid at the zincode now indicated 145·1 grains of acid, to which must be added twenty grains for the saturation of the oxide of the half-equivalent of zinc dissolved, making a total of 165·1 grains of acid, and showing an excess of 6·5 grains over the original quantity in the cell.

The saturation of the acid at the platinode indicated 151·8 grains, or a deficiency of seven grains.

This experiment, therefore, leads to the conclusion that about thirteen grains of acid for an equivalent of water decomposed travelled from the platinode to the zincode; but looking to the number, and indeed the uncertainty, of the processes from which the ultimate quantities were deduced, it ought not, perhaps, to be considered as affording more than a general confirmation of the results previously obtained, viz. that a fourth of an equivalent of sulphuric acid passes from the platinode to the zincode for every single equivalent of a compound which has been electrolyzed by the current.

Allow me here to recall to your recollection your own experiments, in which you compared the quantity of acid transferred from the platinode to the zincode from a mixture of sulphuric acid and water, with the quantity transferred by the same current from a solution of sulphate of soda, and found it in one instance as $\frac{1}{35}$th to $\frac{1}{10}$th, or as 0·027 to 0·100, which very little exceeds one fourth, although from another experiment you obtained somewhat more*.

Experiment 11.—The question now arose, Does the acid, during its transfer in the case of the mixed acid and water, or do the acid and alkali in the case of the saline solution, convey any portion of the current which effects the simultaneous decomposition of the water in both instances?

To answer this question the following arrangement was made. The double cell was charged with a saturated solution of sulphate of soda, and connected with it in the circuit was placed a green-glass tube, into the bottom of which was welded a platinum wire forming the platinode to a portion of chloride of lead, which was kept fused in the tube by means of a spirit lamp. The corresponding zincode was formed of plumbago. The platinum wire before the experiment weighed 5·44 grains. The apparatus conducted well, and chlorine escaped in abundance from the plumbago electrode. When 11·7 cubic inches of hydrogen had been collected from the platinode of the double cell, the experiment was stopped and the results examined.

A well-formed button of lead was found adhering to the platinum wire; and the two together, after having been thoroughly freed from the adhering chloride, weighed 27·1 grains, making the reduced lead 21·66. This is about 4½ grains deficient of the quantity which, adopting the chemical number of lead, it ought to have been to be in proportion to the quarter-equivalent of water, which the hydrogen showed to have been decomposed. The sulphuric acid at the zincode amounted to 9·63 grains, and the soda at the platinode to 7·5 grains, both approaching, respectively, very nearly to 10 and 8, which are the exact equivalent numbers. No manner of doubt can therefore exist, that the same current which is just sufficient to resolve an equivalent of chloride of lead, which is a simple electrolyte unaffected by any associated compound, into its equivalent ions, produces the apparent phenomena of the resolution of an equivalent of water into its elements, and at the same time of an equivalent of sulphate of soda into its proximate principles.

Without this experiment, it might have been supposed that in Experiment 2, the acid, which we know must have passed from the platinode to the zincode of the voltameter at the time of the passage of the hydrogen and oxygen, carried the force which effected the decomposition of the sulphate of soda in the experimental cell; but we may now be certain that this is not the case. The last experiment was repeated with exactly similar results.

It was obviously of great moment to inquire next into the action of the voltaic current on the aqueous solutions of the chlorides, as the simpler constitution of this class of salts promised to throw some light upon the nature of the electrolysis of secondary compounds.

Experiment 12.—A plate of pure tin, whose weight was 375·8 grains, was made the zincode of the double cell, which was charged in all its parts with a strong solution of chloride of sodium. During the passage of the current, not the slightest particle

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* Experimental Researches, § 529.

of gas appeared upon the tin electrode, nor was the slightest smell of chlorine evolved. The experiment was stopped when twenty-four cubic inches of hydrogen had been collected from the platinode. The tin electrode now weighed 346·1, the loss being 29·7 grains, or almost exactly half an equivalent, and corresponding to the quantity of hydrogen evolved. The platinode solution was alkaline and indicated fifteen grains of soda, to which if we add one grain for some soda in the connecting tube, the solution in which was alkaline, we shall have an exact half-equivalent of soda.

Experiment 13.—The last experiment was repeated with the addition to the circuit of a tube containing, as in Experiment 11., fused chloride of lead. The results are stated in the following table, and compared with the exact chemical equivalents:

	Experiment.	$\frac{1}{4}$ equivalent calculated.
Hydrogen evolved . .	12·6	11·8
Lead reduced	24·9	26·0
Tin dissolved	16·3	14·6

The solution in the platinode cell was alkaline, but its saturation was omitted.

Now the simple way of regarding the results of this experiment is, to suppose that, for an equivalent of chloride of lead electrolyzed in the first cell, an equivalent of chloride of sodium was decomposed in the second cell; the chlorine of the latter being absorbed by the tin zincode, and the sodium at the platinode reacting upon the water, and giving rise to the secondary result of an equivalent of hydrogen: upon this hypothesis, the current must have been transmitted by the chloride of sodium alone, and no water was electrolyzed.

Indeed, we must lay it down as a fundamental principle, in discussing the results of all these experiments, that the force which we have measured by its definite action at any one point of a circuit cannot perform more than an equivalent proportion of work at any other point of the same circuit: that the current which we have measured by its electrolyses of an equivalent of simple chloride of lead cannot, at the same time, be sufficient to electrolyze an equivalent of chloride of sodium and an equivalent of water at the same electrodes. The sum of the forces which held together any number of ions in a compound electrolyte could, moreover, only have been equal to the force which held together the elements of a single electrolyte, electrolyzed at the same moment in one circuit.

But how shall we apply this principle to the electrolysis of the solution of sulphate of soda and the results of Experiment 11.? Water seemed to be electrolysed; and, at the same time, the acid and alkali of the salt appeared in equivalent proportion with the oxygen and hydrogen at their respective electrodes. We cannot admit that after the decomposition of the water there was any excess of force applicable to the decomposition of the salt; but we must conclude that the only electrolyte which yielded was the sulphate of soda, the ions of which, however, were not the acid and alkali of the salt, but an *anion* composed of an equivalent of sulphur and four equivalents of oxygen and the metallic *cathion* sodium; from the former, sulphuric acid was formed at the *anode* by secondary action and the evolution of one equivalent of oxygen; and from the latter, soda at the cathode by the secondary action of the metal and the evolution of an equivalent of hydrogen.

These electro-chemical considerations are applicable, of course, to many other saline combinations, as I shall hereafter show; and, in the experiments which I have already detailed, lead to the conclusion that, considered as electrolytes, the following change should be made in the chemical formulæ of the several salts employed.

	Chemical formula.	Electrolytic formula.
Sulphate of soda	$(S + 3\,O) + (Na + O)$	$(S + 4\,O) + Na$
Sulphate of potassa . . .	$(S + 3\,O) + (P + O)$	$(S + 4\,O) + P$
Nitrate of potassa . . .	$(N + 5\,O) + (P + O)$	$(N + 6\,O) + P$
Phosphate of soda . . .	$(P + 2\frac{1}{2}\,O) + (Na + O)$	$(P + 3\frac{1}{2}\,O) + Na$

This view leads me to a modification of the opinion which I have hitherto entertained of the decomposition of sulphate of copper in the constant battery, and the electrolysis of salts, the metallic constituent of which is incapable alone of effecting the decomposition of water at ordinary temperatures. I have always ascribed the appearance of the copper upon the platinode to the secondary action of the hydrogen evolved at that point; but the considerations which I have just submitted to you oblige me to consider it as a primary result of the electrolytic action, the electrolytic formula of sulphate of copper not being $(S + 3\,O) + (Cu + O)$, but $(S + 4\,O) + Cu$. The following experiments were made to elucidate the point still further.

Experiment 14.—The double diaphragm cell was charged at the platinode with a saturated solution of sulphate of copper; the connecting tube and the zincode cell were both charged with dilute sulphuric acid of the standard strength, and a voltameter was included in the circuit. The process was stopped when 35 cubic inches of the mixed gases had been collected. The copper which was precipitated upon the platinode weighed 15·5 grains, and the solution in the platinode cell, which was acid, indicated by neutralization with carbonate of soda, 18·8 grains of free sulphuric acid. The results all approach very nearly to exact equivalent proportions, as shown in the following Table:

	By Experiment. Cubic inches.	By Calculation. Cubic inches.
Oxygen and hydrogen	35	35·4
Precipitated copper	15·5	16
Precipitated sulphuric acid . . .	18·8	20

Experiment 15.—The last experiment was repeated with the substitution of a zincode of zinc for one of platinum: the results are shown in the following Table, and their comparison with the exact equivalent numbers.

	By Experiment. Cubic inches.	By Calculation. Cubic inches.
Oxygen and hydrogen	35	35·4
Precipitated copper	16·7	16
Dissolved zinc	16·4	16
Dissolved sulphuric acid . . .	18·8	20

The appearance of the free sulphuric acid at the platinode cell instead of the zincode is very remarkable. According to the principle which I have laid down, the following view must be taken of the results. The convection of the current in the double cell must have been effected by the electrolysis of the compound electrolyte sulphate of copper $(S + 4\,O) + Cu$, and of the simple electrolyte water $H + O$, the charge being carried by one to its point of junction with the other, and there delivered up to it. If, for convenience, we set out with the sulphate of copper, the metal is deposited upon the platinode, and the compound *anion* $(S + 4\,O)$ travels to the acidulated water, but meeting with nothing with which it can combine, the decomposition of the water commences, the hydrogen of which combines with one equivalent of the oxygen of the compound anion $(S + 4\,O)$, and sulphuric acid $(S + 3\,O)$ remains; the current at the same time passes on with the equivalent oxygen of the water, which is either given off by the platinum zincode or absorbed by the zinc.

Another obvious point of great interest was, to ascertain what relations to the current the products of the electrolysis of the salts of ammonia would exhibit, and I proceeded as follows.

Experiment 16.—The double diaphragm cell, with a tin zincode, was charged with a strong solution of muriate of ammonia, and a voltameter was included in the circuit. The gas from the platinode was collected over mercury. The experiment was stopped when 35 cubic inches of mixed gases had been collected from the voltameter.

No gas was given off from the zincode; but the loss of the tin was 30·4 grains. 23·5 cubic inches of hydrogen were collected from the platinode, and the solution of that cell smelled very strongly of ammonia, and, upon neutralization, was found to contain 8¼ grains of the volatile alkali in a free state. The approximation of these numbers to equivalent proportions will be seen in the following Table:

	From Experiment. Cubic inches.	From Calculation. Cubic inches.
Mixed gases from voltameter	35·0	35·4
Hydrogen from platinode	23·5	23·6
Tin	30·4	29·0
Ammonia	8·25	8·5

Muriate of ammonia, therefore, proved to be an electrolyte whose simple *anion* was chlorine, and compound *cathion* nitrogen with four equivalents of hydrogen. Its electrolytic symbol therefore, instead of being $(C^h + H) + (N\,3\,H)$, would be $C^h + (N + 4\,H)$.

Experiment 17.—The double cell was now charged with a strong solution of sulphate of ammonia, and the experiment conducted as before. Thirty-five cubic inches of mixed gases were collected from the voltameter, 11·5 cubic inches of oxygen from the zincode, and 23·0 cubic inches of hydrogen from the platinode. The zincode solution was acid, and the platinode by neutralization showed eight grains of free ammonia.

	By Experiment. Cubic inches.	By Calculation. Cubic inches.
Mixed oxygen and hydrogen	35	35·4
Oxygen from zincode	11·5	11·66
Hydrogen from platinode	23·0	23·32
Ammonia	8·0	8·5
Sulphuric acid		20·0

To explain these results, we must take into consideration that sulphate of ammonia is not, in a chemical point of view, a mere compound of sulphuric acid and ammonia, but that an equivalent of water is essential to its existence. Its formula is $(S + 3\,O) + (N + 3\,H) + (H + O)$; and by electrolysis it is resolved into one equivalent of sulphur with four equivalents of oxygen given off at the zincode, and one equivalent of nitrogen and four equivalents of hydrogen disengaged at the platinode. As an electrolyte its formula would therefore be $(S + 4\,O) + (N + 4\,H)$. Both the compound *anion* and the compound *cathion* agree perfectly in constitution with those which we have previously found evolved from their combinations with simple substances, at their respective anodes and cathodes.

It is impossible, I think, not to be struck with the singular, and, by me, perfectly unexpected coincidence of the results which I have just detailed with two celebrated hypotheses; the one of BERZELIUS, with regard to the constitution of the muriate of ammonia, and the other of DAVY, concerning the nature of the aqueo-acids and their saline compounds.

The former has been led to imagine, from analogies which it will be quite unnecessary to recapitulate at present, that muriate of ammonia is a chloride of a hypothetical radical, which he has denominated *ammonium*, and which is constituted of one equivalent of nitrogen and of four equivalents of hydrogen; and the oxide of this radical he considers as the basis of the oxysalts of ammonia. According to this view, muriate of ammonia is represented by the formula $(N + 4\,H) + C^h$, and sulphate of ammonia by $(N + 4\,H + O) + (S + 3\,O)$. The former agrees exactly with the conclusion which we have derived from the electrolysis of the salt; but the latter differs from the electrolytic view, which is not that of a combined acid and base, but of *ammonium* and a compound anion $(S + 4\,O)$.

The hypothesis of DAVY was, that the salts of the oxyacids might have an analogous constitution to that of the binary compounds of chlorine and metals, and that the aqueo-acids might be regarded as hydro-acids. As muriatic acid, therefore, is a compound of the simple radical chlorine and hydrogen, or $C^h + H$, aqueo-sulphuric acid may be a compound of a compound radical and hydrogen, or $(S + 4\,O) + H$.

When muriatic acid is brought to act upon soda, water is formed and chloride of sodium, or $C^h + Na$. When aqueo-sulphuric acid is made to act upon soda, water is also formed, and a binary combination of the compound radical and sodium, or $(S + 4\,O) + Na$.

The general view which he propounded was, that a *radical* (which might be either simple or compound, as chlorine or cyanogen, or $(S + 4\,O)$ forms an acid with hydrogen, and a salt with sodium or any other metal. It was supported by many analogies; and it certainly has the advantage of assimilating in constitution a natural group of bodies which resemble one another so closely as the salts, and which former theories separated into the two dissimilar classes of *oxysalts* and *haloid* salts. The progress of organic chemistry, and the doctrine of substitutions, has lately added to the presumptive evidence which favours this hypothesis, and the results of electrolysis which I have just stated will probably be reckoned as direct evidence of its correctness. The only phenomena which do not fall within its comprehension, are those of the decomposition of the dilute sulphuric acid; as there appears no reason why the aqueo-acid should not be resolved into sulphuric acid, and one equivalent of oxygen at the zincode, and hydrogen at the platinode, or $(S + 4\,O) + H$ instead of $\left(\frac{S + 3\,O}{4} + O\right) + H$.

If we regard the water as the electrolyte which yields upon this occasion, it is no less difficult to understand the quarter equivalent of sulphuric acid which accompanies the oxygen to the zincode, and with which the facility of the convection is connected. It is not, however, wholly dependent upon it; for although, as we have seen, the quantity of sulphuric acid which passes is the same in all cases, the facility of electrolyzation decreases as the proportion of acid falls below one part in nine of the mixture.

The formation of these secondary electrolytes, and compound anions and cathions, will probably furnish the key to the explanation of many of those chemical compositions and decompositions to which the presence of water is necessary, such as those of nitric acid with the metals, and to the formation of SCHÖNBEIN's circuit; but the experimental examination of the hypotheses, and of the general question, must be left to a future opportunity. In the mean time,

I remain, my dear FARADAY,
Your faithful friend,
J. FREDERIC DANIELL.

King's College, London,
14th May, 1839.

POSTSCRIPT.

I have since 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 accumulate at the platinode. The amount transferred is in all cases below that of the equivalent of the gases evolved. I am at present engaged in fixing the exact relative proportions, and hope soon to communicate to you the results of my experiments.

J. F. D.

15th June.