

PHILOSOPHICAL TRANSACTIONS.

- I. *Additional Researches on the Electrolysis of Secondary Compounds.* By J. FREDERIC DANIELL, Esq., D.C.L., For. Sec. R.S., Prof. Chem. in King's College, London, and W. A. MILLER, Esq., M.D., Dem. of Chem. in King's College, London.

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THE authors of the following paper having agreed to work together upon the subject of the electrolysis of secondary compounds as opened by one of them, in two letters addressed to Dr. FARADAY, and honoured with a place in the Philosophical Transactions for 1839 and 1840, have arrived at some results, which probably will not be without interest to the Royal Society, and which they have now the honour to communicate.

In the two papers just alluded to, the following points were established. *First.* When aqueous solutions of the neutral metallic salts are exposed to the action of the voltaic current, they are invariably decomposed. When the metal is one of that class which does not decompose water at ordinary temperatures, it is precipitated in the metallic state at the platinode: when it is of the class which does decompose water, its oxide, with an equivalent proportion of hydrogen, appears at the same electrode. The acid at the same time is set free at the zincode, accompanied by an equivalent proportion of oxygen. *Second.* When these results are compared with those of an independent voltameter in the same circuit, it is found that a certain proportion of the force which resolves a single equivalent of a *simple** electrolyte into its anion and cation, produces the resolution of a full equivalent of the *complex* electrolyte into a simple metallic cation and a compound anion. *Third.* When aqueous solutions of ammoniacal salts are electrolysed, similar results are obtained; but instead of a simple metal being disengaged at the platinode, an equivalent of ammonia, accompanied in all cases by an equivalent of hydrogen, appears at the platinode. *Fourth.* We are thus entitled to conclude that in the electrolysis of complex electrolytes, different

* By a simple electrolyte is meant one containing only two elementary substances, being the simplest form of matter capable of electrolysis.

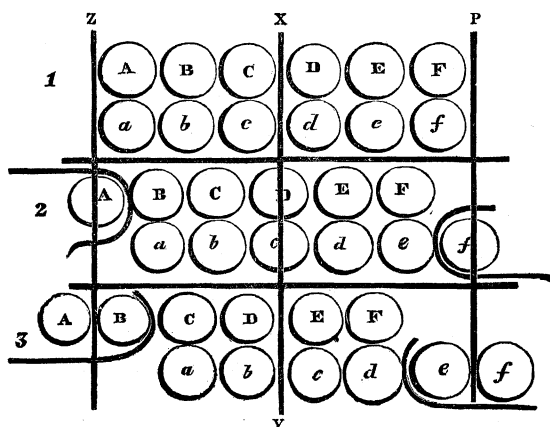
elements travel together under the influence of the voltaic current as compound anions and cations, or as *iso-electric* bodies; that is, groups which are equivalent to each other, and to simple ions, in their relations to the electric forces.

One of the most interesting results of this investigation, was the independent confirmation which it afforded of two celebrated hypotheses, viz. that of DAVY regarding the constitution of aqueo-acids, and the general analogy in the constitution of salts, whether derived from oxyacids or hydro-acids; and that of BERZELIUS concerning the constitution of ammonium.

It was with a view to extend our knowledge of such iso-electric groups, and to trace their connexion with chemical radicles, that we commenced our experiments.

Before we enter upon their detail, it will be best to make a few remarks upon the mode of measuring their results, which has been adopted. It is founded upon the undoubted law of definite electric action; and we have indifferently taken the amount of the ions disengaged at either or both the electrodes by the primary action of the current, or the secondary action of the elements. But there is another mode of effecting this purpose, by a diaphragm cell, in which the products of electrolysis may be kept separate; a method founded upon the hypothesis, that the voltaic decomposition of an electrolyte is not only effected by the disengagement of its anion and cation at their respective electrodes, but by the equivalent transfer of each to the electrodes; so that the measure of the quantity of matter translated to either side of the diaphragm might be taken as the measure of the electrolysis.

This was the mode which was necessarily adopted in the investigation before adverted to, where attempts were made to compare the results of the electrolysis of aqueous solutions of acids* and alkalies† with the simultaneous decomposition of saline solutions. One circumstance, however, was then overlooked, which it is necessary to attend to in making the comparison, viz. that the *disengagement* of whole equivalents of the ions at the electrodes is only accompanied, upon the hypothesis assumed, by the actual *transfer* of half an equivalent to *either* side. This will clearly appear from the following diagram.



* First Letter, p. 108.

† Second Letter, p. 216.

Let A, B, C, &c. in the preceding diagram represent a series of particles of chlorine, *a, b, c, &c.* a series of particles of potassium in combination with the particles of chlorine in the row above them, X, Y a central line or diaphragm, and Z and P the electrodes. If 1 represent the arrangement before the current passes, the particles A and *a, B and b, &c.* being combined to form compound particles of chloride of potassium, 2 would represent the arrangement after a single equivalent of each ion had been disengaged at the electrodes. Each particle would thus necessarily have moved forward half a step, combining with the next adjacent particle, so that B *a, C b, D c, &c.* would now form the chain between the electrodes. If another equivalent be now supposed to be set free at each electrode, one particle of each ion would have passed the central line, one equivalent would thus be *transferred*, whilst two had been *disengaged*, as in fig. 3.

In the instances above referred to, the transfer of one quarter of an equivalent represented half of an equivalent of the hydrates respectively electrolysed. Little stress however need be laid upon this correction, inasmuch as we shall presently show that the hypothesis upon which it is founded, although generally received, is itself destitute of foundation.

1. Our first object was to ascertain more clearly than had yet been done, the influence of water in the aqueous solution of an electrolyte, by comparison with the results of the electrolysis of the same compound when in the state of igneous fusion. It had been already determined, that with regard to the *chlorides* no difference occurred, and that the amounts of chlorine evolved in the same circuit from *fused* chloride of lead*, and from *dissolved* chloride of sodium and muriate of ammonia, were the same†. In the last case, ammonia and hydrogen were evolved at the platinode in equivalent proportions to the chlorine at the zincode. Here a compound cation (NH₄) was separated from an elementary anion.

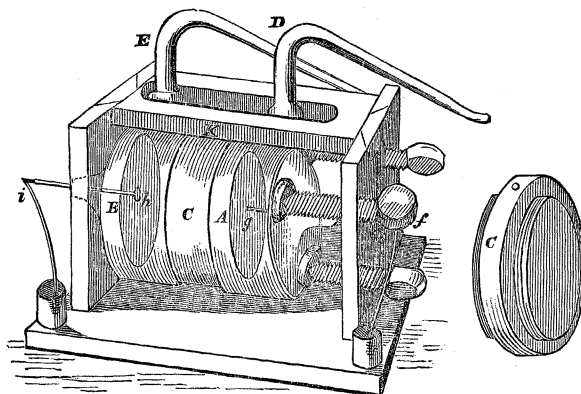
When *nitrate of silver* in solution is subjected to electrolysis, the simple cation, silver, separates from the compound anion (NO₆), and upon substituting the *salt in a state of fusion*, for the solution, we obtained the same result. No gas was evolved, but *crystallized metallic silver* was deposited upon a silver platinode, which gradually increased in length, as it was slowly withdrawn from the liquid salt, just as in the analogous experiment with fused chloride of silver, devised by Dr. FARADAY. Nitrous fumes were at the same time given off from the platinum zincode in abundance. From these experiments it is evident that neither the grouping of a compound cation, nor of a compound anion, is necessarily altered by water in the transit to their respective electrodes.

2. We now turned our attention to that most interesting group of salts, the *phosphates*, which has been so ably discussed by Professor GRAHAM; not without hopes of confirming by electrolysis the beautiful theory of their constitution, which he has

* First Letter, p. 108.

† Ibid. p. 110.

derived from considerations purely chemical. *The double diaphragm cell* which we chiefly employed in these experiments, is represented in the annexed wood-cut.



A and B are the two halves of a stout glass cylinder, accurately ground so as to fit with shoulders liquid tight. C is a hollow ring of glass, also ground on either side, with a flat shoulder to fit against the two half cylinders, which are pressed home by the screws. Each side of the ring is furnished with a rim, which is grooved to admit of a thin piece of bladder being tied over it to form a kind of drum; at K is a small hole to admit of the cavity being filled with a liquid. D and E are two bent tubes, fitted to the two half cylinders for collecting the gases evolved in the experiments. g and h are two circular platinum electrodes connected by wires, i, f (passing through corks in the necks of the half cylinders), with the battery. The apparatus when adjusted forms three compartments, each of which may be filled with the same or a different liquid, and the whole may be supported on a light frame of wood.

We will not attempt to describe the particulars of every experiment referred to in the following pages, for their number is very great, and their details would be both tedious and useless; we will only select some of the principal, in the results of which we can trace no ambiguity; and have no doubt we shall obtain credit for every care in determining the purity of the substances which we employed, and in making the various analyses which were required.

(a.) A strong solution of *tribasic phosphate of soda and water* ($2\text{NaO}, \text{HO}, \text{P}_2\text{O}_5$) (rhombic phosphate) was placed in the platinode cell of the diaphragm apparatus; the centre cell and the zincode cell were both charged with a dilute solution of soda ($\frac{1}{48}$). The power of twenty cells of the small constant battery was transmitted through it, oxygen was evolved at the zincode, and in thirty-seven minutes 48 cubic inches of hydrogen were collected from the platinode; the experiment was then stopped and the solutions examined.

The liquid from the zincode cell was carefully neutralized with nitric acid, and then gave a copious yellow precipitate with nitrate of silver, soluble in nitric acid, and in ammonia, the well-known characters of the tribasic phosphate of silver ($3\text{AgO}, \text{P}_2\text{O}_5$). The solution in the platinode cell had become much more alkaline than at first, but when neutralized with nitric acid, gave a similar yellow precipitate with

nitrate of silver. There could be no doubt therefore that *tritoxyphosphion* (or the radicle of the tritohydrate of phosphoric acid) had travelled to the zincode. The experiment was more than once repeated with unvarying results.

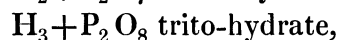
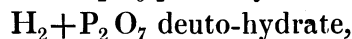
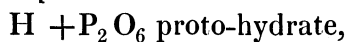
(b.) A solution of *tribasic phosphate of soda* ($3\text{NaO}, \text{P}_2\text{O}_5$) (sub-phosphate) was substituted in the same arrangement for the rhombic phosphate, and, after the action of the battery, on neutralizing the liquid in the zincode cell, a similar copious yellow precipitate was obtained from nitrate of silver.

(c.) To complete the series of tribasic phosphates in which different bases are substituted for each other, a solution of the *phosphate of soda, ammonia and water* $\left(\begin{array}{c} \text{NaO} \\ \text{NH}_4\text{O} \\ \text{HO} \end{array} \right) \text{P}_2\text{O}_5$ (microcosmic salt), was subjected in the same manner to electrolysis, the zincode cell being charged with solution of soda; the solution in the zincode cell became acid to the test of litmus, and produced an abundant yellow precipitate in solution of nitrate of silver; proving that it was the tribasic acid which had travelled as before.

(d.) A similar arrangement was made with a solution of *dibasic phosphate* (pyrophosphate) of soda ($2\text{NaO}, \text{P}_2\text{O}_5$). Hydrogen and oxygen in equivalent proportions were respectively given out at the platinode and zincode, and the process was carried on to the same extent as before. The solution at the zincode after electrolysis was neutralized by nitric acid. When tested with solution of nitrate of silver, a copious white precipitate was formed, indicating that in this case *deutoxyphosphion* (or the radicle of the deuto-hydrate of phosphoric acid) had been transferred to the zincode.

(e.) A solution of *monobasic phosphate* ($\text{NaO}, \text{P}_2\text{O}_5$) (metaphosphate) was subjected to electrolysis under the same circumstances. The solution in the zincode cell was now found to be strongly acid instead of alkaline; when added to a solution of albumen it immediately coagulated it; and with nitrate of silver and nitrate of baryta it produced the characteristic gelatinous white precipitates, which are distinctive of the monobasic phosphates of those bases.

It was thus fully established by these experiments, and confirmed by their repetition, that the three hydrates of the phosphoric acid constitute three essentially distinct acids, which may be expressed as follows:—



and that when disengaged from their corresponding saline compounds by the power of the voltaic current, they travel as three distinct *oxyphosphions* in the circuit. This view, which cannot be doubted as arising from the properties of the acids so disengaged, derives confirmation from the observation that the quantity of acid transferred from the monobasic phosphate of soda was so much greater for the same amount of hydrogen disengaged, than from the dibasic and tribasic salts of the same base.

We had thus the gratification of establishing by independent testimony the correctness of Professor GRAHAM'S theory of the phosphates, and it is with pleasure we also observe that his view of the basic character of water in certain saline compounds is confirmed by the results of the electrolysis of the three tribasic phosphates; from all of which the same acid was separated, notwithstanding that in two instances water obviously constituted one of the three equivalents of base. In our corresponding view, one of the three equivalents of metals was represented by hydrogen.

3. Next in natural order seems to stand the inquiry whether the salts of other tribasic acids would afford analogous results to those of the tribasic phosphates.

(f.) For this purpose we selected the *tribasic arseniate of potassa and water* ($\text{KO}, 2\text{HO}, \text{As}_2 \text{O}_5$) (binarsenate), the platinode cell was charged with a solution of the salt, and the zincode cell and connecting cell with solution of potassa. The combination was found to conduct very well, and oxygen and hydrogen were given off at their respective electrodes. The solution in the platinode cell assumed a grayish appearance, but there was no smell of arseniuretted hydrogen, nor was any arsenic deposited upon the electrode. The solution had become neutral to test paper. The liquid in the zincode cell was carefully neutralized by acetic acid, and afterwards produced in solution of nitrate of silver, the characteristic brick-red precipitate of the arseniate of silver ($3\text{AgO}, \text{As}_2 \text{O}_5$), so that there could be no doubt that the *tritoxarsenion* had travelled into the zincode cell.

The complicated secondary actions which take place in the electrolysis of organic compounds, and which we hope to make the subject of future communications, induce us to abstain at present from extending this part of our inquiry to the organic acids.

4. An inquiry of considerable interest now claims our attention, viz. the electrolysis of salts whose acids, having the same elementary radicle as some of those which have been already examined, are in an inferior degree of oxygenation: such are the arsenites and sulphites.

(g.) A solution of *arsenite of potassa* ($\text{KO}, \text{As}_2 \text{O}_3$) was carefully prepared (by dissolving single equivalents of arsenious acid and bicarbonate of potassa in boiling water), and placed in the platinode cell of the diaphragm apparatus; the connecting cell and the zincode cell were both charged with solution of potassa. During the electrolysis oxygen was given off at the zincode, but an equivalent of hydrogen was not obtained at the platinode, the electrode being covered with metallic arsenic, which was deposited in such abundance as speedily to render the liquid opaque; there was no smell of arseniuretted hydrogen. This diffusion of the metal reduced by secondary action, throughout the solution, contrasts well with the compact manner in which metals are deposited, which, like copper from the neutral sulphate, are thrown down by direct voltaic action. The zincode solution was exactly neutralized by acetic acid; after which a yellow precipitate of the arsenite of silver was produced on adding nitrate of silver.

In this case, as in that of the arseniate just described (3. *f.*), free oxygen was evolved, but the corresponding hydrogen arising from the secondary action of the potassium at the other electrode was taken up in the reduction of the arsenious acid in contact with which it was evolved. No such reduction of the arsenic acid was effected.

It might have been anticipated that the oxygen in travelling with the arsenious acid to the zincode would have combined with it, and formed a portion of arsenic acid; but no such result took place: and it must be remarked, that two equivalents of oxygen instead of one would be required fully to oxidate the whole. We must, therefore, conclude that $\text{As}_2\text{O}_3 + \text{O}$ constitute what we may for the present distinguish as a *sub-oxarsenion*.

The experiment was repeated, by charging all the three cells of the apparatus with the solution of the salt, when oxygen was given off from the zincode as before, and arsenious acid was deposited in white crystals.

(*h.*) The *carbonates* and *oxalates* may be compared together in the same point of view as acids of the same radicle in different states of oxygenation. It has been already stated that in the electrolysis of the former, carbonic acid and oxygen were found to be given off at the zincode in equivalent proportions to the alkali and hydrogen at the platinode; proving those salts to be *oxy-carbions* of the respective metals*. When oxalate of ammonia was treated in the same way, carbonic acid alone was evolved at the zincode, and ammonia with hydrogen at the platinode*. Here the *oxalion* (or sub-oxycarbion) contains the elements of two equivalents of carbonic acid ($\text{C}_2\text{O}_3 + \text{O} = 2(\text{CO}_2)$). In numerous repetitions which we now made of these experiments, we found that although in the electrolysis of oxalate of ammonia ($\text{C}_2\text{O}_3 + \text{O}$) was always exactly evolved, yet that it was not invariably in the form of carbonic acid, but in different proportions of oxalic acid with free oxygen and carbonic acid. It was thus proved that the burning of the oxalic acid into carbonic acid by its associated oxygen was a secondary process, and that the ($\text{C}_2\text{O}_3 + \text{O}$) which travelled in the circuit was in some way different from $2(\text{CO}_2)$.

(*i.*) A similar comparison was then made between the *sulphites* and *sulphates*. In the electrolysis of the latter, it has been shown that sulphuric acid with an equivalent of oxygen (which is evolved) travels to the zincode†. To determine the results of the former, all the cells of the diaphragm apparatus were charged with sulphite of potassa, and a voltameter was included in the circuit; hydrogen was given off from the platinode in exact proportion to that from the voltameter; but no oxygen was evolved from the zincode.

The experiment was by itself ambiguous, for it did not determine whether ($\text{SO}_2 + \text{O}$) travelled as SO_3 , or whether sulphuric acid was formed at the zincode by the secondary action of the oxygen upon the sulphurous acid. Judging from the analogy of the preceding instances, it is most probable that the oxygen with which the sulphurous acid is associated in the *sub-oxysulphion* is in a different state from that of the third

* Second Letter, p. 222.

† First Letter, pp. 107 *et seq.*

equivalent in dry sulphuric acid, and that the sulphuric acid evolved at the zincode in the last experiment is the result of secondary action. Some sulphurous acid was evolved in the zincode cell, which doubtless arose from the action of the sulphuric acid upon the sulphite in contact with which it was produced.

(k.) The experiment was varied by substituting *hyposulphite of soda* ($\text{NaO}, \text{S}_2 \text{O}_2$) for the sulphite, and with analogous results. Hydrogen was given off abundantly at the platinode, but no gas was evolved at the zincode. There was a strong odour of sulphurous acid at the latter, with a gradual deposition of sulphur. This doubtless arose from the secondary action of the sulphuric acid, which was first formed upon the salt with which it was in contact, by which hyposulphurous acid was disengaged, and immediately decomposed. The constitution of the hyposulphite being ($\text{NaO}, \text{S}_2 \text{O}_2$), that of the corresponding sub-oxysulphion would be $\text{S}_2 \text{O}_3$, which if burnt at the zincode would produce $\text{S} + \text{SO}_3$.

5. We now proceeded to apply the method of electrolysis to solve a problem of the same nature as that of the three hydrates of the phosphoric acid, viz. to determine the exact relations of the *yellow and red ferrocyanides of potassium*. It is well known that two views have been taken of the constitution of these two salts: the first represents the yellow salt as a *ferrocyanide of potassium* ($\text{K}_2, \text{Fe Cy}_3$), and the red salt as a *subsesquiferrocyanide* of potassium $\text{K}_3 + 2(\text{Fe Cy}_3)$. The second view represents the two salts as compounds of those metals with two distinct radicles, the former denominated *ferrocyanogen* (Fe Cy_3), the latter *ferridcyanogen* ($\text{Fe}_2 \text{ Cy}_6$). The ferrocyanogen forms a dibasic acid with hydrogen ($\text{H}_2, \text{Fe Cy}_3$), the salts of which are produced by the substitution of two equivalents of the metals for the two equivalents of hydrogen; and the ferridcyanogen forms with hydrogen a tribasic acid ($\text{H}_3 + \text{Fe}_2 \text{ Cy}_6$), with a similar substitution of three equivalents of the metals in their different salts. The real chemical difference, therefore, between the yellow and red ferrocyanides of potassium, consists in the latter containing half an equivalent less of potassium than the former; and so with the other salts from the two classes the metallic elements are in the proportion of 1 to $1\frac{1}{2}$.

Now Mr. PORRETT*, the discoverer of the hydroferrocyanic acid (or as he proposed to call it, the ferro-chyazic acid), long since determined that it travelled in the voltaic circuit by the electrolysis of its salts, to the zincode, the iron accompanying the cyanogen in this transfer, contrary to what might previously have been expected. The question which we now proposed to determine was, whether *ferridcyanogen* as well as *ferrocyanogen* would thus constitute a distinct anion under the directing influence of the battery.

Mr. SMEE † has already determined that the subsesquiferrocyanide of potassium may be formed from the ferrocyanide by the action of the voltaic battery; and has even proposed the process for obtaining the red salt upon a large scale. He, however, explains the change by the action of *nascent oxygen*, which he supposes to be evolved

* Philosophical Transactions, 1814, p. 529.

† Philosophical Magazine, xvii. p. 196.

at the zincode. He observes, "that one equivalent of the yellow *ferrocyanate* is decomposed, the *free potash* travels one way, and the *hydroferrocyanic* acid the other. The oxygen unites with the hydrogen of the acid and sets ferrocyanogen at liberty; this again unites with an equivalent of the *ferrocyanuret of potassium* to form the *ferrosesquicyanuret*." It is evident from this, that this gentleman entertains a very different notion of the steps of the electrolysis to that which we feel justified in supporting, and that therefore he has failed to place it in the point of view to which we propose to adhere.

(*l.*) We commenced our inquiry by carefully repeating Mr. SMEE's experiment in a diaphragm cell, charged throughout with a strong solution of the *yellow ferrocyanide of potassium*. A voltameter was included in the circuit, and the power of twenty cells of the small constant battery was employed. Gas was evolved at the platinode, which was tested and found to be pure hydrogen; it was in equivalent proportion to the gases in the voltameter. No gas was at first evolved at the zincode, but the solution in that cell became gradually red, particularly at the surface. When 4 inches of hydrogen had been collected at the platinode a slight disengagement of gas commenced at the zincode, which continued, and proved to be oxygen, and was in the proportion of one-third of the gas from the platinode. After 16 cubic inches had been collected from the platinode, we stopped the experiment and examined the results.

The platinode solution was much paler than before, and was alkaline. The zincode solution was deep green and acid, and the zincode plate was covered with a slight film of Prussian blue. Crystals of the red ferrocyanide separated from the zincode solution by spontaneous evaporation, and when the evaporation was complete, a radiated mass of a purplish-brown colour was obtained: on solution a small quantity of Prussian blue remained, and the solution had lost its acid reagency. The addition of acetate of lead to the solution produced but a scanty precipitate, proving the quantity of yellow ferrocyanide remaining in it to be but small.

The explanation of these results is, we think, sufficiently obvious. Ferrocyanogen was doubtless transferred to the zincode, and potassium to the platinode, the former combined with a portion of the ferrocyanide to form the subsesquiferrocyanide; the process being accelerated by the abstraction of a portion of the potassium passing over to the platinode, where by its reaction upon the water of the solution it was converted into potassa with the evolution of hydrogen. As the process proceeded more ferrocyanogen was given off at the zincode than could be absorbed by the yellow salt; and it consequently began to react upon the water, becoming converted by the abstraction of its hydrogen into hydroferrocyanic acid, its oxygen being evolved. The acid reaction is thus accounted for, as well as the deposition of Prussian blue, from the well-known spontaneous decomposition of the acid.

(*m.*) This experiment was several times repeated with variation of the quantities, but with substantially the same results. The evolution of oxygen from the zincode

was hastened by narrowing the dimensions of the electrode, which thus presented a smaller surface for the reaction of the ferrocyanogen upon the ferrocyanide. When the process was continued for a long time, yellow crystals of the ferrocyanide were formed in the platinode cell. Upon subsequent trial it was found that a strong solution of potassa produced a similar deposit, under ordinary circumstances, in a solution of the yellow salt. It will probably be objected, that although the red ferrocyanide is thus obviously formed by secondary action, yet where once formed it may be capable of decomposition as an electrolyte, in which ferridcyanogen acts as the anion. The following experiment however is decisive against such a view.

(*n.*) The diaphragm cell was charged throughout with a strong solution of *the red salt*, the purity of which had been tested. The solution was deep green by reflected light, but red by transmitted light. The power of the same constant battery was applied to it, and the platinode solution very quickly changed its colour and became yellow. When 5.75 cubic inches of hydrogen had been collected from the platinode the yellow colour was perfectly pure; the action was then stopped. The liquid at the zincode was of a very dark brown-green colour, and strongly acid, it had a pungent peculiar smell, the liquid soon became perfectly opaque, and one cubic inch of oxygen was collected from the zincode. Though the colour of the two solutions in the electrode cells had undergone such marked changes, the colour of that in the intermediate cell remained unaltered. The liquid from the platinode cell yielded on evaporation tabular crystals of the yellow ferrocyanide, and when hydrate of potassa was added to the zincode solution, a yellow colour was developed.

Here then we obviously have the converse results of the last experiments; or the formation of ferrocyanide of potassium from subsesquiferrocyanide by the abstraction of half an equivalent of ferrocyanogen transferred from the platinode to the zincode.

(*o.*) Could a doubt remain with regard to the conclusion to be derived from these experiments, it must be removed by the results of the following arrangement. The zincode cell was filled with a dilute solution of potassa, and the connecting cell with the same. The platinode cell was charged with a strong solution of the red ferrocyanide. This solution previously to the commencement of the experiment gave no blue solution with perchloride of iron. The liquid in the zincode and connecting cells speedily became yellow, and after a short time the solution in the platinode cell also became yellow. All the solutions were now found to contain the yellow ferrocyanide. Thus it was quite clear that no such compound as ferridcyanogen travelled from the red salt when exposed to electrolysis, but that the red salt was converted into the yellow by the abstraction of ferrocyanogen from the platinode, which ferrocyanogen being transferred to the zincode, there formed with the potassium presented to it by electrolysis the same yellow ferrocyanide.

In order to extend further our knowledge of the electrolysis of this class of secondary compounds, the following experiments were made:—

(*p.*) A diaphragm apparatus was charged with a strong solution of *cyanide of po-*

tassium (K, Cy) in the platinode cell, and a solution of potassa in the zincode and connecting cells. The arrangement conducted well; gas was given off from both electrodes, and cyanide of potassium formed in abundance in the zincode cell. Hydrogen must therefore have been given off at the platinode by the oxidation of the potassium evolved, and oxygen at the zincode by the deoxidation of potassa under the influence of the current in the formation of the cyanide of potassium.

(*q.*) The apparatus was charged throughout with solution of cyanide of potassium, and subjected to the current. Gas was given off as before at the platinode; but at first none from the zincode. The liquid in the zincode cell gradually became of a deep brown colour, and the electrode itself was coated with a deep brown matter, which was easily washed off. In the latter part of the operation gas was also evolved in small quantity at the zincode. The solution smelled strongly of hydrocyanic acid, of which, by the proper tests, it was found to contain a considerable quantity. There can be no doubt that the brown matter which was abundantly formed was *para-cyanogen*, which is soluble in the alkaline solution of the cyanide of potassium, and which must have been produced either by the spontaneous decomposition of the hydrocyanic acid, or in a way something analogous to the formation of the red ferrocyanide of potassium from the yellow by the absorption of an additional quantity of ferrocyanogen.

(*r.*) A diaphragm apparatus was charged throughout with *sulphocyanide of potassium* (K, S₂ Cy). Upon the first application of the current the action was brisk, but soon declined, and when 5½ cubic inches of gas had been collected from the platinode and 1½ cubic inch from the zincode it ceased. There was a copious orange-coloured deposit in the zincode cell and upon the plate which interrupted the progress of the electrolysis; no particular odour was perceptible in either of the cells. The liquid filtered from the zincode became turbid by exposure to the air, and deposited more of the yellow compound. The clear liquid was again subjected to the current, which it transmitted readily, and with the same phenomena as before. There could be little doubt that *sulphocyanogen* was the anion transferred in this experiment. This part of our subject still presents a tempting field for investigation, from which however we were for a time diverted by an important class of facts which next fell under our observation; we have however since returned to the study, and are at present engaged in researches upon the cobaltocyanides, and other double cyanides, the results of which we hope ere long to lay before the Society.

6. We were purposing to follow up the examination of the double salts by the electrolysis of other classes of these compounds, when we were stopped by the occurrence of a new order of phenomena, which it was necessary to turn aside and examine as affecting the very foundation of the process which we were employing. In our examination of the phosphates, our plan had been to transfer by electrolysis the acid of the salt placed in the platinode cell into a solution of potassa placed in the zin-

code cell for its reception, and then to determine its quantity and its properties from those of the salt which was formed by secondary combination.

The arrangement which we now made was to place the salt at the zincode with the view of passing its bases into an acid at the platinode. We commenced our experiments with the double sulphates with the view of comparing the different hydrates of the sulphuric acid with the hydrates of the phosphoric acid already examined, and throwing more light upon the results of the electrolysis of the dilute acid.

(s.) Some pure *sulphate of potassa and copper* ($\text{CuO}, \text{SO}_3, + \text{KO}, \text{SO}_3$) was carefully prepared, and its solution placed in the zincode and connecting cells of the diaphragm apparatus: the platinode cell was charged with dilute sulphuric acid, the current of twenty cells of the battery was transmitted through the arrangement until 48 cubic inches of hydrogen had been collected from the platinode, and 23.5 cubic inches of oxygen from the zincode (about one equivalent in grains), when the process was stopped. The platinode solution was perfectly colourless with a very slight deposit of copper upon the platinode, amounting only to 0.1 grain. It was evaporated to dryness in vapour of ammonia, and the residue was perfectly white sulphate of potassa, which weighed 21 grains. It was entirely soluble in water: and ammonia did not produce the slightest blue colour in its solution. The liquids of the zincode and connecting tubes together required 51 grains of dry carbonate of soda to neutralize the free acid. Now, it will be observed, that the sulphate of potassa was only one grain less than a quarter of an equivalent, which considering the nature of the processes by which these quantities were determined, will appear a very near approximation; and we may take the results of the electrolysis to have been as follows:— For one equivalent of force as measured by the gases evolved at the zincode and platinode, half an equivalent of oxysulphion of potassium (sulphate of potassa) was decomposed (as measured by the quarter equivalent potassium transferred), and half an equivalent of oxysulphion of hydrogen (aqueous sulphuric acid): for it will be observed, as most remarkable, that the quantity of copper transferred was perfectly insignificant.

Upon the view of the principle of electrolysis hitherto commonly admitted, viz. definite decomposition with equivalent and opposite transfer of the elements or radicles of the compound to the opposite electrodes of the battery, these results were sufficiently perplexing: but our perplexity increased as we proceeded; and it was not till after we had expended an incredible amount of labour in testing different hypotheses of various resistances and opposing forces, supposed to be developed in these complicated cases, that we thought of questioning the principles themselves. These abortive attempts we shall not, of course, obtrude upon the Society, but proceed to select such experimental evidence as may be sufficient to establish, in as concise a manner as possible, the conclusions to which we have arrived.

(t.) A solution of *sulphate of alumina and potassa* (alum) ($\text{Al}_2 \text{O}_3, 3\text{SO}_3$) + (KO, SO_3)

was subjected to exactly the same treatment as the preceding double salt, and the results were precisely similar. 48 cubic inches of hydrogen were collected from the platinode. When ammonia was added in excess to the solution in the platinode cell no precipitate was produced, which proved the absence of alumina. Evaporated to dryness, the saline residue was ignited, and weighed 21 grains. It was sulphate of potassa, and the amount, as before, was within one grain of the quarter of an equivalent.

(u.) Some of the double *sulphate of magnesia and potassa* ($\text{MgO}, \text{SO}_3, + \text{KO}, \text{SO}_3$) was carefully prepared, and submitted in solution to the same treatment. After 48 cubic inches of hydrogen had been collected the platinode solution was evaporated to dryness, and left a saline residue of 36.6 grains. This was redissolved and treated with carbonate of potassa. A precipitate of carbonate of magnesia was thus obtained, which was reconverted into sulphate, and weighed 3.8 grains; this was equivalent to 0.76 grain of magnesium, to which must be added 0.24 grain recovered from the wash water by means of phosphate of ammonia, making the total quantity of magnesium which had passed over to the platinode 1.0, or about $\frac{1}{2}$ th of an equivalent. Deducting the total amount of sulphate of magnesia, 4.98 grains, from the mixed sulphates, 36.6 grains, we have 31.62 as the amount of the sulphate of potassa.

Thus it appeared that the three bases, alumina, magnesia, and oxide of copper, or their metals, when in combination with sulphuric acid and potassa, refused to travel from the zincode to the platinode under the influence of the voltaic current into an acid with which they were capable of forming an immediate and soluble combination. Could it be that the same results might follow from the electrolysis of the single salts of the same acid?

(w.) Some pure *sesquisulphate of alumina* ($\text{Al}_2 \text{O}_3, 3\text{SO}_3$) was prepared by precipitating alum with excess of ammonia, thoroughly washing the precipitate and redissolving it in sulphuric acid, with the aid of heat. An excess of alumina was left, from which the liquid was separated by filtration. It was then evaporated till it solidified upon cooling. The mass was subjected to pressure in calico, and the dry salt dissolved in water.

The zincode and connecting cells of the diaphragm apparatus were then charged with the solution, and the platinode cell with dilute sulphuric acid. The arrangement conducted well, and in half an hour 13 cubic inches of oxygen were collected from the zincode. The process was then stopped, and on supersaturating the liquid at the platinode with ammonia, the slightest possible trace of alumina was precipitated.

Thus it again appeared that the electrolysis was carried on without the transfer of the base or its metal to the platinode.

Was the peculiar constitution of this salt as a *sesqui* compound concerned in any way in this result?

(x.) A salt of the same order, viz. the *sesquisulphate of iron* ($\text{Fe}_2\text{O}_3, 3\text{SO}_3$), was prepared with great care, and its solution treated exactly in the same way as the last. It conducted well, and 13 cubic inches of oxygen were collected from the zincode in twenty-eight minutes. On neutralizing the liquid of the platinode cell with ammonia, very slight traces of sesquioxide of iron appeared. The sesquioxide of iron had therefore resisted the transfer as well as the sesquioxide of aluminum.

(y.) We next tried salts of the more ordinary constitution of single equivalents of acid and base. The zincode and connecting cells were charged with solution of *sulphate of copper* (CuO, SO_3), and the platinode cell with dilute sulphuric acid. The combination conducted well, 23.6 cubic inches of oxygen were collected from the zincode, and an equivalent of hydrogen from the platinode; but the platinode plate was scarcely covered with a very thin film of copper, the metal not having been transferred in any considerable quantity. Upon neutralizing the solutions on the two sides by carbonate of soda, it was found that an equivalent of sulphuric acid had travelled to the zincode. Upon reversing the arrangement, oxygen was collected as before from the zincode, and an equivalent of copper was thrown down upon the platinode, but no hydrogen was evolved.

(z.) The last experiments were varied by the substitution of solution of sulphate of potassa for the dilute sulphuric acid in combination with the sulphate of copper. When the copper solution was placed at the zincode, none of the metal passed over to the platinode, but a full equivalent of hydrogen was collected with alkali and acid at their respective electrodes. When the position of the two salts was reversed, the potassium travelled into the platinode cell, and was at once indicated by a precipitate of hydrated oxide of copper. The platinode plate was also covered partly with coherent copper, and partly with pulverulent metal, and only 3 cubic inches of hydrogen were collected for 71 cubic inches of mixed gases in the independent voltameter. None of the copper solution had penetrated to the zincode cell.

Thus it appeared that copper refused to exchange places with potassium in the circuit, as it had before refused to exchange with hydrogen, and so to pass from the zincode to the platinode.

(a. a.) *Sulphate of zinc* (ZnO, SO_3) was next subjected to the same treatment, and the results were exactly similar; the metal in all cases refusing like the copper to pass from the zincode division of the diaphragm cell to the platinode in any considerable quantity.

To ascertain whether the passage of the current from one electrolyte to another was in any way concerned in preventing the transfer of the base, we now resolved to employ *sulphate of copper* in solution *throughout* the whole arrangement, and having carefully ascertained the proportion of copper in solution, we placed 1500 grains of the liquid in each cell; metallic copper was thrown down on the platinode, and on precipitating the oxide from the liquid in the cell by potash, we found exactly the same amount of copper (taking the united quantities obtained from the oxide preci-

pitated, and from the metal deposited) as before the experiment. An equivalent of sulphuric acid was set free at the zincode, but the quantity of the copper solution in the cell continued the same as at the commencement. Copper thus appeared to refuse to exchange with itself in electrolysis.

Sulphate of zinc afforded results exactly similar.

(*a. b.*) That the diaphragm itself did not throw any obstruction in the way of such transfer we satisfied ourselves, by varying its substance, from membranes to porous earthenware; but this was put out of all doubt in the following manner. A long siphon tube reversed was filled with a strong solution of sulphate of copper, and two strips of copper were made the electrodes of the battery; the action proceeded very slowly, but after a long time the liquid in the platinode limb of the apparatus became sensibly lighter-coloured, while that in the zincode became darker; the oxysulphion disengaged at the latter point had dissolved the copper of the zincode, which, however, had no power to pass to the platinode, to replace the metal which had there been deposited.

The preceding experiments bear closely upon an observation familiar to persons engaged in electrotyping on the large scale, viz. that the solution around the platinode becomes impoverished, and at last nearly deprived of copper.

As it appears to be thus established, that in the electrolysis of complex electrolytes, the metals which are capable of decomposing water at ordinary temperatures, or whose oxides are largely soluble in water, are susceptible of transference in the voltaic circuit from the zincode to the platinode, whilst those which are not marked by this strong affinity for oxygen remain stationary; we were anxious to ascertain to which class ammonium belongs.

(*a. c.*) The apparatus was charged with a solution of *muriate of ammonia* ($\text{NH}_4 \text{Cl}$) of known strength throughout; 35.5 cubic inches of hydrogen were collected from the platinode; the zincode liquid was yellow and smelt strongly of chlorine. By careful neutralization with muriatic acid, it was ascertained that an equivalent quantity of ammonia had been disengaged in the platinode cell, and by precipitation of the chlorine with nitrate of silver, from the liquid thus neutralized, we found that the solution contained the same amount of chlorine as before the experiment; the amount of ammonium in combination with it, must, therefore, have remained unchanged: it had received no addition by transfer from the zincode side. The results of the experiment were perfectly clear and decisive.

(*a. d.*) In an experiment which was made in the same manner with *microcosmic salt* (NaO , $\text{NH}_4 \text{O}$, HO , $\text{P}_2 \text{O}_5$), the sodium travelled to the platinode, but the whole of the ammonium remained in the zincode cell. Here a *polybasic* acid was used, and yet results similar to those with a monobasic acid obtained. We have still further evidence that the nature of the acid does not appear to be connected with this travelling of the base, from the fact, that when the double *tartrate of soda and ammonia*

($\left. \begin{matrix} \text{NaO} \\ \text{NH}_4\text{O} \end{matrix} \right\} \text{C}_8 \text{H}_4 \text{O}_{10}$), was electrolysed, putting a solution of soda into the platinode cell, the sodium was found to have travelled, but ammonium had refused to do so, as in the other cases already mentioned.

It was thus ascertained, contrary to the anticipations which we had formed upon its extreme solubility, that ammonium is included in that class of basic compounds which refuse to travel in the voltaic circuit.

(*a.e.*) To show that a relation exists between the power of transference in the circuit, and the affinity of the oxides of the metals, for water, the results of three experiments may be taken with salts of potassa, baryta and magnesia. For one equivalent of force as measured by 71 cubic inches of mixed gases from the voltameter,

14.2 grains of potassium = $\frac{1}{3}$ equivalent were transferred from sulphate of potassa into sulphuric acid.

11.5 grains of barium = $\frac{1}{6}$ equivalent, were transferred from nitrate of baryta into a solution of the same salt.

1.0 grain of magnesium = $\frac{1}{12}$ equivalent, was transferred from sulphate of magnesia into sulphuric acid.

The experiments are not rigidly comparable together, nor must the quantities be taken as absolute determinations of the amount of each metal which travels in the circuit, but only as indicating a dependence of the transfer upon the attractive power of water or its elements.

The supposed anomalous transfer of sulphuric acid in the electrolysis of its mixture with water, the investigation of which cost so much labour upon a former occasion*, is now easily accounted for upon the hypothesis of the unequal transfer of the oxysulphion and hydrogen of the hydrate to their respective electrodes.

We were next induced to seek for some such connexion between the attraction of the different *acids* for water, and their transfer to the zincode. Our experiments had already embraced a great variety of acids, differing very much from one another in this respect, and in every case the transfer had taken place; but our attention had not yet been directed to the quantitative results.

(*a.f.*) As tungstic acid forms no definite hydrate and is insoluble in water, we selected it as an extreme test of the fact, and for this purpose prepared some pure *tungstate of soda* (NaO, WO_3) by fusing together equivalent quantities of the acid and carbonate of soda. The product of the operation was dissolved and crystallized. A solution was made which contained one-twentieth of its weight of the salt; it was placed in a diaphragm apparatus, and was found to conduct badly. The current was transmitted for $1\frac{3}{4}$ hour, when the zincode liquid was found to be distinctly acid, owing to the formation of a soluble bitungstate, and the platinode very strongly alkaline. Upon precipitating the tungstic acid from both sides, by hydro-sulphuret of

* Second Letter, p. 222.

ammonia and nitric acid, it was decidedly shown that a portion of the acid had travelled to the zincode cell.

Neutral *chromate of potassa* (KO, CrO_3), which contains an acid forming no definite hydrate with water, furnished a perfectly analogous result; and the same thing was observed in the experiments with *arsenite of potassa*.

(*a. g.*) The carbonic acid is one of those which seems to have the least affinity for water, but it has been already shown that in the electrolysis of the carbonates of potassa, soda and ammonia, it is given off as oxy-carbion at the zincode in equivalent proportions. We now repeated the experiment. The diaphragm cell was charged throughout with *carbonate of soda* (NaO, CO_2) of definite strength, and the gas tube from the zincode cell connected with a drying apparatus, and LIEBIG'S bulbs. The amount of carbonic acid was ascertained by weighing the bulbs, and by careful precipitation of the liquid in the cell by caustic ammonia and chloride of barium. By these means it was ascertained that there had been a decided transfer of the acid to the zincode, though in much less proportion than that of the sodium to the platinode. From the quantities of acid transferred in these experiments (which quantities however, as they can be considered but approximations to accuracy, we have not thought it necessary to record), it would appear that those acids which form no definite hydrates, are transferred to the zincode in smaller quantity than is the case with those from which distinct hydrates are obtainable.

(*a. h.*) We were extremely anxious to devise some means of ascertaining the phenomena of transfer in the case of simple electrolysis, but were forced to abandon the attempt after many trials, from the difficulty of procuring any substance which would answer the purpose of a permeable diaphragm, whilst it could resist the heat which is necessary to bring the chlorides, or similar binary compounds into the liquid state. We, however, ascertained that when a solution of *chloride of sodium* in water was electrolysed, the chlorine was transferred to the zincode in greater quantity than the sodium from it.

(*a. i.*) To remove the possibility of its being thought that water in these experiments conveyed the force independently of the presence of the saline bodies (a supposition hardly reconcilable with the phenomena observed where the saline solution was used throughout the apparatus), the following experiments were made. The platinode cell of the diaphragm apparatus was charged with dilute sulphuric acid, and the zincode with distilled water; one diaphragm alone was employed. The arrangement conducted so badly, that in an hour and a half, with twenty cells of the battery, only 1.5 cubic inch of hydrogen was collected from the platinode. The apparatus was then recharged and the electrodes reversed, the water being now at the platinode, and the acid at the zincode. In an hour and a half 2.8 cubic inches of hydrogen were collected from the platinode. From the imperfect conducting power evinced by water in these and other experiments, we can hardly suppose that the current, in cases where the base is not transferred, is carried by the electro-

lysis of this fluid, mysterious and ill-understood as its electrical relations undoubtedly are.

7. In reviewing the results which we have obtained from the preceding experiments, and the conclusions which we are entitled to draw from them, it will, we think, be admitted that many of them are of the highest interest and importance, and some of them at variance with the fundamental principles of electrolysis which have been hitherto admitted.

We have seen that in every instance, the definite action of the electric current is maintained; and its passage through a compound liquid conductor is always marked by the disengagement at the platinode of hydrogen or the metallic element, or else of a group of substances, like ammonium, constituting an equivalent compound; and the simultaneous disengagement at the zincode of the non-metallic element, or a group of substances of iso-electric powers. Of such electrolytes it may be convenient to distinguish the following classes:—

1st. An electrolyte may consist of *simple ions*, and then must be constituted of a single equivalent of a metal (or H) for its cation, and a single equivalent of a non-metallic element for its anion; as K, I; Ag, Cl; &c.; they may be termed *simple electrolytes*.

2nd. An electrolyte may consist of a *compound cation*, a single equivalent of which must take the place of a metal; and a single equivalent of a *simple non-metallic anion*, as NH_4 , Cl. Organic alkalies probably form compound cations of this nature, and when their salts are electrolysed, hydrogen is always disengaged with them at the platinode, as with ammonia; these and the following we may call *complex electrolytes*.

3rd. An electrolyte may consist of a *compound anion*, a single equivalent of which would take the place of the simple non-metallic anion, with a single equivalent of a *simple cation*, a metal (or H), as H, NC_2 ; K, SO_4 ; Na, NO_6 .

4th. An electrolyte may consist of a single equivalent of a *compound cation*, and a single equivalent of a *compound anion*, as NH_4 , SO_4 .

These four cases may be included in the term *Monobasic Electrolytes*, as a single equivalent of force (measured by the voltameter) would electrolyse single equivalents of the electrolytes.

5th. An electrolyte may also consist of *two or more equivalents of a metallic cation* or (H), or of *single equivalents of two or more metallic cations* (or H); when the *anion* must consist of a *single equivalent of a compound ion*, as $(\text{K}_2 \text{FeCy}_3)$. This compound ion, in the case of an oxysalt, contains the so-called anhydrous acid in combination with as many equivalents of oxygen as there are of metallic cations (or H) in the compounds, as $(\text{Na}_3, \text{P}_2 \text{O}_5, \text{O}_3)$.

In this case as many equivalents of force will be required for the electrolysis of one equivalent of the electrolyte as there are equivalents of metal (or H) in the cation. They may be denominated *Polybasic Electrolytes*.

In these compound anions and cations, it would appear that the oxygen which travels with the acid group, and the hydrogen which is evolved with the alkaline group, must be connected with the other elements whilst under the influence of the current in a manner differing from that in which the latter are combined together; for we have found that in most cases this connection is immediately dissolved upon their escape from the electric influence, whilst in some others their apparent permanent combination is only the effect of secondary action, where the oxygen is capable of forming a chemical compound of a higher degree of oxygenation, and like other secondary actions of a similar nature, is variable in its amount.

8. The disengagement of the cation and anion of an electrolyte in equivalent proportions is not always effected, as is commonly represented, by their simultaneous transfer in opposite directions to their respective electrodes, in the exact proportion of half an equivalent of each; but is sometimes brought about by the transfer of a whole equivalent of the anion to the zincode, whereby a whole equivalent of the cation is left uncombined at the platinode; or by transfer of unequivalent portions of each in opposite directions, making however together a whole equivalent of matter transferred to one electrode or the other; or speaking more correctly, *by the transfer of a quantity of matter capable of exerting one equivalent of chemical force*, so that when the anion *transferred* to the zincode exceeds half an equivalent, the cation transferred to the platinode is in an equal proportion less than half an equivalent, and *vice versa*; the anion and cation *set free* being always in equivalent proportions. We have, however, in no case observed the transfer of a whole equivalent of the cation to the exclusion of the anion.

These facts are, we believe, irreconcilable with any of the molecular hypotheses which have hitherto been imagined to account for the phenomena of electrolysis, nor have we anything more satisfactory at present to substitute for them; we shall therefore prefer leaving them to the elucidation of further investigation, to adding one more to the already too numerous list of hasty generalizations.