XL. Additional researches on the electrolysis of secondary compounds

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which equality of products of factors, taken in opposite orders, does *not* in general hold good for quaternions ($j^2 = -i^2$); the *commutative* character of ordinary multiplication is therefore in general *lost* in passing to the new operation, and $Q Q' - Q' Q$, instead of being a symbol of zero, comes to represent a pure imaginary, but not (in general) an evanescent quantity. On the other hand, for quaternions as for ordinary factors, we may in general *associate the factors among themselves, by groups, in any manner which does not alter their order*; for example,

$$Q \cdot Q' Q'' \cdot Q''' Q^{IV} = Q Q' \cdot Q'' Q''' Q^{IV};$$

this, therefore, which may be called the *associative* character of the operation, is (like the distributive character) *common* to the multiplication of quaternions, and to that of ordinary quantities, real or imaginary.

[To be continued.]

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

[Continued from p. 188 and concluded.]

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 zincode 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 dry-

ness, 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 $\frac{1}{10}$ 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 precipitated, 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* (NH_4Cl) 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 , NH_4O , HO , P_2O_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* $\left(\begin{smallmatrix} \text{NaO} \\ \text{NH}_4\text{O} \end{smallmatrix} \right) \text{C}_8\text{H}_4\text{O}_{10}$ 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

* Second Letter, p. 222.

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 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 hy-

drates, 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 electrolysis 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 alkalis 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 versâ*; 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 phænomena 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.

XLI. *On an improved Method for the Detection and Quantitative Determination of Arsenic.* By REMIGIUS FRESENIUS, M.D.*

THE greater part of this paper is occupied with the discussion of the medico-legal questions arising in cases of poisoning; the author advocates the interference of the legislature to render it imperative on chemists to pursue a given method in seeking for the presence of poisons: and after pointing out the sources of uncertainty in all the methods employed hitherto for the detection of arsenic, he proposes a new one, which he alleges is free from every objection, which method is the result of many investigations pursued by himself in conjunction with Dr. von Babo.

* Communicated by the Chemical Society; having been read April 15, 1844.