

Somewhat similar experiments have also been made with glass tubes with negative results.

The author has also made a few experiments to ascertain the influence of a voltaic current in increasing or diminishing the flow of hydrogen through the medium, but so much depends upon the structure of the metallic surfaces in contact with the medium and their relative sizes, as well as upon the electromotive force, &c., of the battery used, that this subject would probably require somewhat elaborate researches.

The author, however, hopes to make further investigations into the nature of the movements of hydrogen produced in vitreous matters and in metals.

II. "On the Electrolysis of Dilute Sulphuric Acid and other Hydrated Salts." By J. H. GLADSTONE, Ph.D., F.R.S., and ALFRED TRIBE, Lecturer on Chemistry in Dulwich College. Received December 20, 1883.

On the 1st of March last a communication was presented to the Royal Society by Professor Frankland, in which, among other things, the reactions we had described as taking place in the charging and discharging of secondary batteries were confirmed. The author expressed these reactions, however, by formulæ founded on the electrolysis, not of H_2SO_4 , but of hexabasic sulphuric acid, H_6SO_6 , in accordance with the views of Bourgoin.

The point of difference is a small one, but it led us to look into the papers of Bourgoin, and to examine the evidence upon which his views were based. The French chemist ("Ann. de Chimie," 1868) treats of the electrolysis of sulphuric acid merely as an illustration of his method for determining the composition of hydrated salts in solution generally. This method consists in electrolysing a given solution in a divided cell, analysing the liquid in each compartment at the close of the experiment, and, in the case of dilute sulphuric acid, collecting the hydrogen set free. In the case of a solution of sulphuric acid, of course, the positive compartment may be expected to increase in strength as a consequence of the electrolytic action, and the negative compartment to decrease in strength in the same degree. Bourgoin calls the increase of the acid in the positive compartment α , and concludes that 2α represents the amount of sulphuric acid electrolysed. This conclusion rests on the well-known theoretical views of Grotthuss, and, did his theory express all that goes on in the electrolytic process, the method would readily discriminate between the actions represented by the following formulæ:

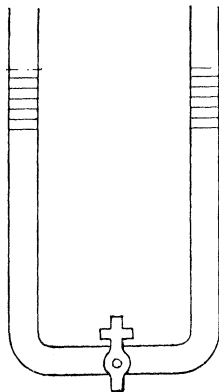
VOL. XXXVI.

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Before Electrolysis.		After Electrolysis.	
		Positive pole.	Negative pole.
(1.)	$\text{SO}_3\text{H}_2\text{O}$	$= \text{SO}_3 + \text{O}$	H_2
(2.)	$\text{SO}_33\text{H}_2\text{O}$	$= \text{SO}_3 + \text{O}_3$	H_6
(3.)	$\text{SO}_3n\text{H}_2\text{O}$	$= \text{SO}_3 + \text{O}_n$	H_{2n}

But it was pointed out by Reuss, as far back as 1807, that when electrolytic action occurs across a permeable diaphragm, a portion of the liquid may travel from the positive to the negative compartment of the compound cell by what is now called electrical endosmose. Daniell and Miller ("Phil. Trans.," 1844) pointed out that in electrolytic action there was also an unequal transference of the ions. It is evident that each of these actions must introduce additional terms into the formula with which Bourgoin worked. Moreover, Daniell ("Phil. Trans.," 1839) investigated the electrolysis of sulphuric acid of very different strengths by a similar method, and in a review of the evidence ("Phil. Trans.," 1840) concluded that for each equivalent of hydrogen liberated, the acid which passed across the diaphragm was not more than one-fourth nor less than one-fifth of an equivalent. Most of his experiments incline to the former. Did 2α , therefore, represent the amount of sulphuric acid electrolysed, it would appear from his results that *tetra*-, and not *hexa*-, basic sulphuric acid was decomposed by the current. Again, Hittorf, in 1853 (*vide* Wiedemann's "Electricity," vol. ii, p. 589), observed that for one equivalent of hydrogen liberated, the amount of sulphuric acid which was found in the positive compartment varied, but not regularly, with the strength of the acid. These discrepancies, both of observation and deduction, led us to make some experiments on the subject ourselves.

The apparatus we employed consisted of a U-shaped tube of about 70 cub. centims. capacity, having a stop-cock in the centre of the horizontal part. The vertical parts of the apparatus were divided into millimetres, and the hole in the stop-cock packed with asbestos.



We found that the closeness of the packing could be so nicely adjusted as scarcely to allow mechanical admixture of the fluids, on the one hand, or electrical endosmose on the other. In our experiments we varied the current density, and, unlike Bourgoin ("Annales de Pharmacie," vol. xv), found that the increase of sulphuric acid in the positive compartment per equivalent of hydrogen set free decreased along with the decrease in the current density. The strength of acid was 4·2 per cent. The results are set out in the annexed table.

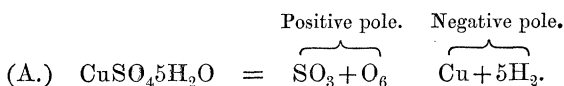
Current in milli-ampères.	Time in hours.	Increase of sulphuric acid in positive compartment for one part of hydrogen set free.
32·8	20	9·17
33·4	6	9·5
72·3	2·5	10·3
72·7	2	9·4
106	2	11·0
117	2·5	10·5
215	1·5	12·05
220	1	12·04
229	2	12·31

It is necessary also to bear in mind the remarkable phenomenon called by the Germans "Wanderung der Ionen." Daniell long ago described an experiment in which he placed dilute sulphuric acid in the positive compartment and a solution of sulphate of copper in the negative. He found that when 15·5 grs. of copper had been deposited on the negative electrode there were 23 grs. of sulphuric acid in the same compartment. Now, as 15·5 grs. of copper are equivalent to 24 grs. of sulphuric acid, and as Bourgoin's formula allows for the formation of only half an equivalent of sulphuric acid, that is 12 grs., it is evident that there was a considerable accumulation of that substance unaccounted for. In two similar experiments made with our apparatus, we obtained for 0·147 and 0·125 grm. of deposited copper respectively 0·209 and 0·180 grm. of free sulphuric acid. The half equivalents would be 0·114 and 0·097 grm. respectively. The excess of acid in all these cases is due to the "unequal transference of the ions." If both compartments had been filled with sulphuric acid, some similar transference would doubtless have taken place, in addition to what is expressed in Grotthuss' chain of decomposition.

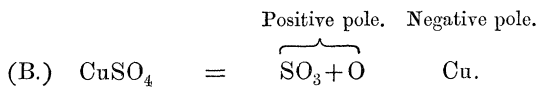
We conclude, therefore, from our own results, as well as from those of previous experimenters, that the method employed is incapable of determining whether it is H_2SO_4 or some hydrate which yields to the current.

Copper Sulphate.

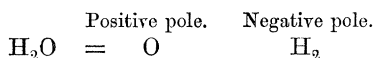
A careful examination of the chemical changes which accompany the electrolysis of a solution of copper sulphate appeared, however, capable of throwing additional light on the value of this electrolytic method for ascertaining the composition of hydrates in aqueous solution. It is well known that water forms with CuSO_4 a definite hydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The anhydrous salt is white, the hydrate blue. It is reasonable to suppose that the blue solution of this salt contains molecules of this or of some higher hydrate. Now, if in the electrolytic process the water of hydration suffers decomposition along with the CuSO_4 , the primary chemical changes might be expected to be—



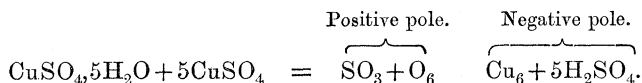
But, if the water of hydration takes no more part in the electrolysis than the water of solution does, then the chemical changes would manifestly be—



Of course the collateral action—



might also take place, but this would occur only with currents of considerable density. The method is obviously capable of discriminating between these two actions, even supposing a considerable quantity of the electrolyte travelled unchanged from one compartment of the apparatus to the other. For, in the first case, either free hydrogen would be liberated at the negative pole, or free acid formed in the negative compartment, equal to five-sixths of the total copper deposited; the free acid, and the five-sixths of the total copper, to which it is equivalent, being produced by the chemical action— $5\text{H}_2 + 5\text{CuSO}_4 = \text{Cu}_5 + 5\text{H}_2\text{SO}_4$; equation A becoming—



On the other hand, if the action was in accordance with B there would be only a deposition of copper on the negative electrode, and no formation of free acid in the negative compartment. In the annexed table the results and particulars of several experiments are set out. In each experiment 25 cub. centims. of a 10 per cent.

solution of sulphate of copper were placed in the negative and positive compartments respectively of the apparatus. The positive electrode consisted of a platinum wire, and the negative of a weighed strip of metallic copper.

Experiment.	Time in hours.	Free sulphuric acid.	
		Pos. Compartment.	Neg. Compartment.
I.	1½	·0766	nil.
II.	2	·0936	nil.
III.	3	·1868	·0191
IV.	3	·1501	·0204
V.	3	·2442	·0237
VI.	3	·2546	·0372

In none of these experiments was there any trace of hydrogen visibly escaping from the negative electrode, while, as will be seen from the table, there was no free acid formed in the negative compartment till two hours or more had elapsed. By that time some admixture in the horizontal part of the apparatus might reasonably be expected, and even in the greatest instance it is small as compared with the amount of salt decomposed.

Similar experiments were made with the sulphate of zinc, with similar results, no hydrogen being evolved, and little or no sulphuric acid appearing in the negative compartment.

We conclude, therefore, that it is not possible to determine the composition, or even to show the presence of a hydrated salt in aqueous solution by means of this electrolytic method.

III. "On the Dynamics of a Rigid Body in Elliptic Space."
By R. S. HEATH, B.A., D.Sc., Fellow of Trinity College, Cambridge. Communicated by A. CAYLEY, LL.D., Sadlerian Professor of Pure Mathematics in the University of Cambridge. Received January 4, 1884.

(Abstract.)

This paper is an attempt to work out the theory of the motion of a rigid body under the action of any forces, with the generalised conceptions of distance of the so-called non-Euclidean geometry. Of the three kinds of non-Euclidean space, that known as elliptic space has been chosen, because of the perfect duality and symmetry which exist in this case. The special features of the method employed are