

PROFESSOR H. BUFF ON THE LAW OF ELECTROLYSIS.

VI.—*On the Law of Electrolysis.*

BY PROFESSOR H. BUFF.

The law of definite electrolytic decomposition, if not hitherto decidedly opposed, has yet been regarded as doubtful by many physicists. Others have considered it only as approximatively true; among those inclined to this view are Martius,* Schoenbein,† de la Rive,‡ &c. Jacobi, who as late as last year published some experiments on the electrolysis of sulphate of copper,§ is disposed to consider that the intensity of the action depends on the concentration of the solution. The celebrated discoverer of the electrolytic law has admitted, in the 12th series of his experimental researches on electricity, that fluid electrolytes may possibly conduct currents under a certain strength, without being decomposed by them; and that this conducting power, though not equal in different fluids capable of decomposition by electricity, yet in all cases obtains only in very weak currents.

As definite electric decomposition, if rigorously proved, presents a capital method of determining the unit of electricity, inasmuch as this unit would then become identical with the unit of chemical action, it appeared to me of great interest to ascertain by accurate measurements the limits between which the law of Faraday holds good. From the results of an investigation undertaken for this purpose, I consider it as proved, that even the smallest amount of electricity cannot pass through a liquid, capable of being decomposed, without producing an equivalent amount of decomposition.

According to the view generally adopted at present, I regard as electrolytes all chemical compounds which, like water, hydrochloric acid, chloride of lead, &c., consist of an electro-positive radical, which under galvanic influence collects at the negative electrode, and of an electro-negative radical, which is disengaged at the positive electrode. Thus sulphate of copper consists of the positive radical Cu and the negative one SO_4 ; nitrate of silver of the positive radical Ag and the negative NO_6 ; sulphate of ammonia of the positive radical NH_4

* Pogg. Ann. LVIII, 284; Inst. 1850, 30.

† Pogg. Ann. XLIII, 238.

‡ Pogg. Ann. LIV, 403.

§ Petersb. Acad. Bull. IX, 333.

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the negative one SO_4 , &c. According to this view, the electrolytic action remains the same whether the current liberates an equivalent of hydrogen from water, or an equivalent of the radical NH_4 from a salt of ammonia. The question which I proposed to solve was, whether this action is only attendant on currents of certain strength, or whether it takes place proportionately with the weakest currents.

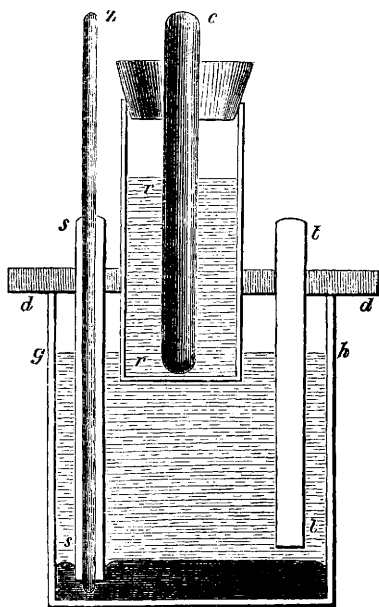
In order to apply very weak currents to electrolytic processes, and yet to separate a quantity of substance sufficient for weighing, it was necessary that a galvanic battery should be arranged as to give a weak but perfectly constant current, for some days at least. None of the known batteries answered this purpose. But as this want of uniform action in the so-called constant batteries arises more from deteriorating influences, than from the principle of their construction, I tried to obviate the former as much as possible, and I succeeded best by a modification of Daniell's battery. A little loss of power is produced in this battery by the zinc being gradually converted by the surrounding acid into sulphate of zinc.

This evil may, however, as is well known, be easily avoided by filling the zinc cell at once with sulphate of zinc. It is true that the resistance to conduction is increased in this way, but this is scarcely worth consideration with a current which has to traverse a long distance. The principal cause of variation in Daniell's battery when currents of long duration but small power are required, is caused by the copper solution gradually passing over by endosmosis into the zinc solution. Not only is copper precipitated chemically by this means, and consequently the equivalent amount of zinc lost for the process; but the copper precipitated on the surface of the zinc of course alters the state of the surface of the electro-positive metal, while it gives rise at the same time to secondary currents, which hasten the precipitation of copper and consequent loss of zinc.

These local currents are moreover the cause of the deposition of copper in the pores of the cells, and of its appearing even on the outer surface of the same.

By the following contrivance, of which the accompanying sketch represents a section, the influence of endosmosis was reduced to a minimum.

A glass vessel with ground edges is provided with a well-fitting cover *dd*, having three apertures, into which are introduced three glass tubes. The middle one *rr*, which should be as wide as possible, is closed at the lower end with bladder; of the two other tubes, *ss* and *tt*, the tube *ss* descends into a layer of mercury covering the



bottom of the vessel, while the other *tt* has its lower aperture at the sulphate of zinc, so that the liquid moistens the porous diaphragm of the tube *rr*. In this tube a solution of sulphate of copper, together with some crystals, is introduced. By introducing a strip of copper *c* into the tube *rr*, and a piece of zinc *z* into the tube *ss*, and connecting *c* with *z*, by means of a conductor, a perfectly constant current is produced, inasmuch as the mercury continually dissolves as much zinc as is necessary to keep up a steady action. Endosmosis is certainly not quite prevented by this arrangement; but it takes place very slowly, the zinc solution being more dense

than that of the copper. As the lower extremity of the zinc is dissolved by the mercury, the rod gradually falls. In order to facilitate the renewal of the sulphate of copper, without deranging the current, the strip of copper is held in its place by a cork, which half fills the opening. The tube *tt* serves to remove from time to time a little sulphate of zinc by means of a pipette, and to replace what is removed by water. Batteries of this description have been in use since the middle of July, without their action having varied, up to the 1st of October, and without the necessity of disconnecting them; towards the middle of the latter month, a slight diminution of the current was perceptible. Upon closer examination, it was found to have arisen from a deposition of oxide of iron in the pores of the bladder, which was otherwise perfect.

Although this battery when in action presents a considerably greater resistance to conduction than the ordinary Daniell's battery, it is nevertheless well adapted for working the electric telegraph, and I have no doubt that, when once applied to this purpose, it will replace all other arrangements.

The advantages it possesses over the ordinary Daniell's battery may be easily seen from the following experiment. One element of the latter was connected with one wire of a galvanometer by means

of two wires of equal length. A deflection of 78° was produced on the galvanometer. A second element of the modified construction, when connected with the other wire of the galvanometer, caused a deflection of $77^\circ.5$.

When both currents were passed simultaneously, but in opposite directions, through the coil of the galvanometer, a deflection of $8^\circ.5$ was produced in favour of Daniell's battery. This decreased in two hours to 8° , in twenty hours to $7^\circ.5$, and continued constantly diminishing. After nine days, the Daniell's battery only caused a deflection of 33° , while that of the modified arrangement remained constant at $77^\circ.5$.

The equivalent of zinc electrolytically consumed for a current of this strength, during an action of 13085 minutes' duration, is 164.6 milligrammes. The actual amount consumed in the constant battery, however, was 1140 milligrammes, or 7 times that quantity, while in Daniell's battery, 27700 milligrammes, or 168 times the quantity of zinc were consumed. These great losses were occasioned by local actions, and would consequently appear less considerable with stronger currents. The constant battery described above has been exclusively used for the following experiments. One and the same pair served throughout the whole investigation, which lasted several months, without its being necessary to disconnect them once; nothing was done to them excepting that from time to time small pieces of sulphate of copper were added.

To determine the relation which the electrolytic action bears to the strength of current, I employed a neutral solution of nitrate of silver. In this were immersed two strips of chemically pure silver, so that under the influence of the battery, silver was dissolved from one strip, while it was deposited upon the other. For the pure metal, as well as for a perfectly pure and neutral solution of nitrate of silver, I am indebted to the kindness of Professor von Liebig, who prepared both himself expressly for this investigation. The alteration of the strength of the current was effected by interposing wires of various lengths. For this purpose I employed two copper wires, perfectly equal and very thin, of such a length that each presented a resistance to conduction equal to that caused by a silver wire of 1.5 millimetres in thickness and 1,800,000 metres in length. It is evident that, in comparison to such an immense resistance, that of the galvanic element, together with that of the decomposing cell, would form only a small fraction. Both were, however, specially measured, and it was found that together they only were equal to $\frac{1}{130}$ th of that produced by the whole length of wire. According as the wires r and r

were introduced successively, or singly, or both together (representing a wire of double section) into the galvanic circuit, three currents were produced, the strength of which bore almost exactly the proportion of 1 : 2 : 4. The weight of silver electrically deposited bore the same proportion, as will be seen from the following table :

Resistance of the wire.	Duration of current.	Weight of deposited silver in milligrammes :	
		Found.	Calculated for 6000 minutes.
$r + r'$	2547 minutes	55·5	130·74
r	1393 „	60·1	258·87
r'	1411 „	60·95	259·17
$\frac{r + r'}{4}$	720 „	62·2	518·33

The weakest current employed was capable of precipitating in 100 hours 130·74 milligrammes of silver. The equivalent amount of hydrogen is 1·2 milligrammes, or 13·42 cub. cent., which quantity would therefore have been liberated by the same current in 100 hours. This gas being somewhat soluble in water, as well as in acids and in solutions of salts, it is evident why the electrolysis of water by weak currents has escaped observation, and why some physicists have been led to believe that water can conduct small quantities of electricity without suffering decomposition.

In order to ascertain whether the decomposing power of weak currents is the same in different parts of the circuit, two cells filled with silver solution of the same composition were connected by the whole length of wire $r + r'$ with the constant battery. The current was passed with unvarying strength for nearly 9 days, or 12538 minutes. The following were the results :

- 1st. cell. Loss of weight of the positive silver strip = 267 mllgrms.
 Gain of weight of the negative silver strip = 266·6 „
 2nd. „ Loss of weight of the positive silver strip = 267·6 „
 Gain of weight of the negative silver strip = 267·4 „

1 cub. cent. of the solution employed contained 25 milligrammes of neutral nitrate of silver.

To ascertain whether the state of concentration of the fluid had any influence, a more dilute solution was prepared, of which 1 cub. cent. contained 10 milligrammes of salt. Two cells filled with these solutions were introduced, together with the wire r , into the circuit. The experiment lasted 51·5 hours. After this time, the negative strip of silver in the stronger solution had gained 124·66 milligrammes in weight ; while the corresponding strip in the more dilute solution had

gained 124·16 milligrammes. The state of dilution has therefore no influence on the results of the electrolysis.

To obtain comparative results, it is necessary that the solutions should be perfectly pure.

Less silver is apparently deposited from acid solutions than is required by the law, and in alkaline solutions of cyanide of silver, some of the precipitated silver is also redissolved.

When the weakest current was employed, that is, when the whole length of wire $r+r'$ was included, the amount of silver dissolved in 10 hours was greater than that deposited. Acid solutions of sulphate of copper likewise yield, on galvanic decomposition, too little copper; this is caused by the simultaneous action of the atmospheric oxygen and of the free acid on the negative copper plate.

When a galvanic current was passed at the same time through a perfectly pure neutral solution of sulphate of copper, and through a solution of nitrate of silver, the results of the electrolysis of these two solutions showed a close coincidence in the metals deposited. The following are a few of the numbers obtained:

Duration of experiment in minutes.	Amount of silver in milligrammes.	Amount of copper:		Strength of current.
		Found.	Calculated.	
2669	107·4	33·9	31·44	1·85
1236	534·5	157·9	156·5	19·88
1397	683·85	200·6	200·2	22·5
1029	535·7	157·6	156·82	24·5
458	862·4	257·8	252·5	86·6

The strength of the current produced when the whole length of wire $r+r'$ was introduced, has been assumed as the unit of strength. After each experiment was ended, the copper was deposited on a strip of platinum, was freed from adhering sulphate by washing with boiled water, and then dried *in vacuo* over concentrated sulphuric acid. It was always covered with a thin coating of suboxide, from which it was freed by ignition in a current of hydrogen. In order to prevent this oxidation of the copper as much as possible during the experiment, the solution was previously freed from air. Some decompositions were effected entirely under the air-pump. During the experiment, hydrogen was frequently passed through the solution; none of these precautions were however quite effectual. Even that copper which had been ignited in hydrogen, and was consequently perfectly pure, soon became covered with a thin film of oxide, sometimes even during the time occupied in weighing.

The facility with which galvanically deposited copper absorbs oxygen from the air, is the reason why in all cases a little more copper was obtained than corresponds to the equivalent of silver.

It would scarcely be possible to prove the law of definite electrolytic action with other bodies capable of galvanic decomposition as readily as with copper- or silver-salts. I consider myself however justified in concluding, from the foregoing experiments, that wherever deviations from the law have been observed, they have been caused by local actions, which, however, it may not always be possible to obviate.
