

XXII. *Experiments on the chemical Production and Agency of Electricity.* By William Hyde Wollaston, M. D. F. R. S.

Read June 25, 1801.

NOTWITHSTANDING the power of Mr. VOLTA'S electric pile is now known to be proportional to the disposition of one of the metals to be oxidated by the fluid interposed, a doubt has been entertained by many persons, whether this power arises from the chemical action of the fluid on the metal, or, on the contrary, whether the oxidation itself may not be occasioned by electricity, set in motion by the contact of metals that have different conducting powers.

That the oxidation of the metal is the primary cause of the electric phænomena observed, is, I think, to be inferred from the following experiments, which exhibit the GALVANIC process reduced to its most simple state.

Exper. 1. If a piece of zinc and a piece of silver have each one extremity immersed in the same vessel, containing sulphuric or muriatic acid diluted with a large quantity of water, the zinc is dissolved, and yields hydrogen gas, by decomposition of the water: the silver, not being acted upon, has no power of decomposing water; but, whenever the zinc and silver are made to touch, or any metallic communication is made between them, hydrogen gas is also formed at the surface of the silver.

Any other metal beside zinc, which by assistance of the acid employed is capable of decomposing water, will succeed

equally, if the other wire consists of a metal on which the acid has no effect.

Exper. 2. If zinc, iron, or copper, are employed with gold, in dilute nitric acid, nitrous gas is formed, in the same manner, and under the same circumstances, as the hydrogen gas in the former experiment.

Exper. 3. Experiments analogous to the former, and equally simple, may also be made with many metallic solutions. If, for instance, the solution contains copper, it will be precipitated by a piece of iron, and appear on its surface. Upon silver merely immersed in the same solution, no such effect is produced; but, as soon as the two metals are brought into contact, the silver receives a coating of copper.

In the explanation of these experiments, it is necessary to advert to a point established by means of the electric pile.

We know that when water is placed in a circuit of conductors of electricity, between the two extremities of a pile, if the power is sufficient to oxidate one of the wires of communication, the wire connected with the opposite extremity affords hydrogen gas.

Since the extrication of hydrogen, in this instance, is seen to depend on electricity, it is probable that, in other instances, electricity may be also requisite for its conversion into gas. It would appear, therefore, that in the solution of a metal, electricity is evolved during the action of the acid upon it; and that the formation of hydrogen gas, even in that case, depends on a transition of electricity between the fluid and the metal.

We see, moreover, in the first experiment, that the zinc, without contact of any other metal, has the power of decom-

posing water; and we can have no reason to suppose that the contact of the silver produces any new power, but that it serves merely as a conductor of electricity, and thereby occasions the formation of hydrogen gas.

In the 3d experiment also, the iron by itself has the power of precipitating copper, by means, I presume, of electricity evolved during its solution; and here likewise the silver, by conducting that electricity, acquires the power of precipitating the copper in its metallic state.

The explanation here given receives additional confirmation from comparative experiments which I have made with common electricity; for it will be seen, that the same transfer of chemical power, and the same apparent reversion of the usual order of chemical affinities in the precipitation of copper by silver, may be effected by a common electrical machine.

The machine with which the following experiments were conducted, consists of a cylinder 7 inches in diameter, with a conductor on each side, 16 inches long, and $3\frac{1}{2}$ inches diameter, each furnished with a sliding electrometer, to regulate the strength of the spark received from them.

Exper. 4. Having a wire of fine silver, $\frac{3}{120}$ of an inch in diameter, I coated the middle of it, for 2 or 3 inches, with sealing-wax, and, by cutting through in the middle of the wax, exposed a section of the wire. The two coated extremities of the wire, thus divided, were immersed in a solution of sulphate of copper, placed in an electric circuit between the two conductors; and sparks, taken at $\frac{1}{10}$ of an inch distance, were passed by means of them through the solution. After 100 turns of the machine, the wire which communicated with (what is called) the negative conductor, had a precipitate formed on its surface, which,

upon being burnished, was evidently copper; but the opposite wire had no such coating.

Upon reversing the direction of the current of electricity, the order of the phenomena was of course reversed; the copper being shortly redissolved by assistance of the oxidating power of positive electricity, and a similar precipitate formed on the opposite wire.

Exper. 5. A similar experiment made with gold wires $\frac{1}{100}$ of an inch diameter, in a solution of corrosive sublimate, had the same success.

The chemical agency, therefore, of common electricity, is thus proved to be the same with the power excited by chemical means; but, since a difference has been observed in the comparative facility with which the pile of VOLTA decomposes water, and produces other effects of oxidation and de-oxidation of bodies exposed to its action, I have been at some pains to remove this difficulty, and can at least produce a very close imitation of the GALVANIC phenomena, by common electricity.

It has been thought necessary to employ powerful machines, and large Leyden jars, for the decomposition of water; but, when I considered that the decomposition must depend on duly proportioning the strength of the charge of electricity to the quantity of water, and that the quantity exposed to its action at the surface of communication depends on the extent of that surface, I hoped that, by reducing the surface of communication, the decomposition of water might be effected by smaller machines, and with less powerful excitation, than have hitherto been used for that purpose; and, in this hope, I have not been disappointed.

Exper. 6. Having procured a small wire of fine gold, and

given it as fine a point as I could, I inserted it into a capillary glass tube; and, after heating the tube, so as to make it adhere to the point and cover it in every part, I gradually ground it down, till, with a pocket lens, I could discern that the point of the gold was exposed.

The success of this method exceeding my expectations, I coated several wires in the same manner, and found, that when sparks from the conductors before mentioned were made to pass through water, by means of a point so guarded, a spark passing to the distance of $\frac{1}{8}$ of an inch would decompose water, when the point exposed did not exceed $\frac{1}{700}$ of an inch in diameter. With another point, which I estimated at $\frac{1}{1500}$, a succession of sparks $\frac{1}{2}$ of an inch in length, afforded a current of small bubbles of air.

I have since found, that the same apparatus will decompose water, with a wire $\frac{1}{40}$ of an inch diameter, coated in the manner before described, if the spark from the prime conductor passes to the distance of $\frac{4}{10}$ of an inch of air.

Exper. 7. In order to try how far the strength of the electric spark might be reduced by proportional diminution of the extremity of the wire, I passed a solution of gold in *aqua regia* through a capillary tube, and, by heating the tube, expelled the acid. There remained a thin film of gold, lining the inner surface of the tube, which, by melting the tube, was converted into a very fine thread of gold, through the substance of the glass.

When the extremity of this thread was made the medium of communication through water, I found that the mere current of electricity would occasion a stream of very small bubbles to rise from the extremity of the gold, although the wire, by which it communicated with the positive or negative conductor, was

placed in absolute contact with them. Hence it appears, that decomposition of water may take place by common electricity, as well as by the electric pile, although no discernible sparks are produced.

The appearance of two currents of air may also be imitated, by occasioning the electricity to pass by fine points of communication on both sides of the water; but, in fact, the resemblance is not complete; for, in every way in which I have tried it, I observed that each wire gave both oxygen and hydrogen gas, instead of their being formed separately, as by the electric pile.

I am inclined to attribute the difference in this respect, to the greater intensity with which it is necessary to employ common electricity; for, that positive and negative electricity, so excited, have each the same chemical power as they are observed to have in the electric pile, may be ascertained by other means.

In the precipitation of copper by silver, an instance of de-oxidation (or phlogistication) by negative electricity has been mentioned: the oxidating power of positive electricity may be also proved, by its effect on vegetable blue colours.

Exper. 8. Having coloured a card with a strong infusion of litmus, I passed a current of electric sparks along it, by means of two fine gold points, touching it at the distance of an inch from each other. The effect, as in other cases, depending on the smallness of the quantity of water, was most discernible when the card was nearly dry. In this state, a very few turns of the machine were sufficient to occasion a redness at the positive wire, very manifest to the naked eye. The negative wire, being afterwards placed on the same spot, soon restored it to its original blue colour.

By Mr. VOLTA'S apparatus, the same effects are produced in much less time.

Beside the similarity which has thus been traced between the effects of electricity excited by the common machine and those observed from the electric pile, I think it appears also probable, that they originate from the same source.

With regard to the latter, its power is now known to depend on oxidation; so also does the excitement in the former appear very much to depend on the same process; for,

Exper. 9. I have found, that by using an amalgam of silver or of platina, which are not liable to be oxidated, I could obtain no electricity. An amalgam of tin, on the contrary, affords a good degree of excitement. Zinc acts still better; but the best amalgam is made with both tin and zinc, a mixture which is more easily oxidated than either metal separately.

Exper. 10. But, as a farther trial whether oxidation assists in the production of electricity, I mounted a small cylinder, with its cushion and conductor, in a vessel so contrived that I could at pleasure change the contained air.

After trying the degree of excitement in common air, I substituted carbonic gas, and found that the excitement was immediately destroyed, but that it returned upon re-admission of atmospheric air.

In conformity to this hypothesis, we find that the metal oxidated is, in each case, in a similar state of electricity; for the cushion of the machine, by oxidation of the amalgam adhering to it, becomes negative; and, in the same manner, zinc oxidated by the accumulated power of an electric pile, or simply by action of an acid, is also negative.

This similarity in the means by which both electricity and GALVANISM appear to be excited, in addition to the resemblance that has been traced between their effects, shews that they are both essentially the same, and confirms an opinion that has already been advanced by others, that all the differences discoverable in the effects of the latter, may be owing to its being less intense, but produced in much larger quantity.