

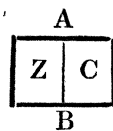
XXIX. *An experimental examination of the electric and chemical theories of galvanism.* By WILLIAM RITCHIE, A.M. F.R.S., Rector of the Royal Academy at Tain.

Read May 7, 1829.

1. **T**HE continental philosophers still continue to adopt the electric theory of galvanism proposed by VOLTA, whilst those in Britain as uniformly follow some modification of the chemical theory proposed by Dr. WOLLASTON. From this diversity of opinion we may safely conclude, that the experimental proofs for the truth of either theory are not sufficiently powerful, to command the assent of all capable of appreciating the weight of such evidence. I have therefore ventured to lay before the Society the following experiments and observations; as they appear to me to establish the truth of some modification of the chemical theory, and to demonstrate the fallacy of the principles on which the electric theory rests.

2. The fundamental principle assumed by VOLTA, and supported by his followers, is, that if dissimilar metals be brought into contact they are instantly thrown into opposite electric states. This he conceives to be a new law of nature, and claims to himself the honour of the discovery. He conceives that its truth is proved by the following experiment.

Let Z be a plate of zinc, and C a plate of copper, soldered together at the line of contact A B. Hold the plate of zinc in the hand, and touch the under plate of a delicate electric condenser (le condensateur à lames d'or) with the copper plate, whilst a moistened finger is applied to the upper plate of the instrument. Remove the compound plate and the moistened finger, and then lift the upper plate of the instrument by its insulating handle, and the slips of gold leaf will be found to diverge. Taking for granted the truth of the experiment, the conclusion which VOLTA deduced from it by no means follows as a legitimate inference. Dr. WOLLASTON has shown that a galvanic effect is produced by dissimilar metals with the moist



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air of the atmosphere acting as a chemical agent and an imperfect conductor. The same fact is proved by the electric column of DeLuc. The plate of zinc becomes partially oxidized by the oxygen of the atmosphere, electricity is generated or set at liberty, and the film of moist air in contact with the two metals acts as the fluid conductor in an ordinary voltaic arrangement. If the compound plate be coated with electric cement to exclude the chemical action of the air on the zinc, I will venture to predict that no decided electric effect will take place. Until the supporters of the electric theory show by direct experiment that electric effect does take place with this modification of the apparatus, we must view the whole of their reasoning as founded on a gratuitous supposition. Having thus shown that VOLTA and his followers have overlooked what appears to me to be the very cause of the disturbance of electric equilibrium in the two metals, I shall now demonstrate that the other principle on which the theory is built is equally unfounded. This will appear obvious from the two following experiments.

EXPERIMENT I.

Having poured into a watch glass a quantity of diluted sulphuric acid, I placed on the surface of the fluid a piece of gold leaf, which was connected with one of the cups of a delicate galvanometer. I then placed a disc of platina foil in the fluid below the gold leaf, and connected it with the other cup of the instrument; scarcely any electro-magnetic effect was produced. Having removed the acid, I substituted water containing condensed chlorine: a very decided electro-magnetic effect was produced. A similar effect was produced by using nitro-muriatic acid, or aqua regia as it was formerly called, instead of the chlorine. The needle of the galvanometer in both cases turned round in the same direction as it does when zinc was substituted for the gold leaf and copper for the platina. Having tried, by the common method, the conducting powers of the diluted sulphuric acid and the water containing chlorine, I found that the diluted acid was the most powerful conductor. When the preceding experiment was repeated with discs of zinc and copper instead of discs of gold and platina, I found that the most powerful effect was produced when the diluted sulphuric acid was used. This experiment clearly proves that the interposed fluid does not act merely as a conductor to the electricity excited by

the imaginary electro-motive force, since in the first case the electricity generated is greatest when the conducting power of the fluid is least.

EXPERIMENT II.

Having made a small rectangular box divided into two equal compartments by a diaphragm of bladder, I introduced into one of them a disc of hard copper, and into the other an equal disc of soft copper. These discs being connected with the cups of the galvanometer, and the chambers filled with water, a considerable galvanic effect was produced, and the needle turned round as it does when the place of the hard copper was supplied with a disc of zinc. I then poured a little nitrous acid into the chamber containing the hard copper, and observed that the effect was diminished. By adding a little more acid the needle turned round several degrees in the opposite direction. This experiment completely overthrows the assumed principle that the galvanic effect increases with the conducting power of the fluid interposed between the metallic plates, since by increasing the conducting power of the fluid the effect was diminished, and by a proper increase was completely destroyed. It is a curious fact, that if nitric, sulphuric, or muriatic acid be used instead of the nitrous, the results will be quite the reverse.

Having thus, I trust, satisfactorily shown that the electric theory is founded on false principles, I shall now very shortly examine the truth of the most generally received chemical theory of galvanism.

3. Dr. WOLLASTON assumes that positive electricity is set at liberty by the combination of oxygen with one of the metals. This principle is frequently true, but in many cases it is totally false. This will be rendered obvious by the following experiments.

EXPERIMENT III.

Immerse two equal discs of zinc, connected by wires with the galvanometer, into the chambers of the rectangular box formerly used, and fill both compartments with water; no action will of course take place. Pour a little sulphuric, nitric, or muriatic acids into one of the chambers, a considerable galvanic effect will be produced, and the needle will turn in the same direction as it does when copper is substituted for the plate of zinc immersed in the chamber

containing the water alone. This agrees with the chemical theory. Again, instead of the above acids use nitrous acid, and the needle will turn round in the opposite direction. The same thing holds when discs of copper or iron are employed. This is completely at variance with the chemical theory, since that plate is negative, or corresponds with copper in the standard battery, on which the greatest chemical action of the fluid takes place. The following experiment is also hostile to the generally received theory.

EXPERIMENT IV.

Having taken two pieces of block tin, I cut the surface of one of them into ridges by means of a three-cornered file, so that the surface was doubled. With these two pieces I formed a binary combination, and immersed them in diluted nitro-muriatic acid; a very considerable electro-magnetic effect was produced, and the needle turned round in the same direction as it does when a plate of zinc is substituted for the plane disc in the standard battery. It is obvious that there must be a greater chemical action between the acid and the furrowed plate than the other, and yet the furrowed plate corresponds with copper in the standard battery, on which the least chemical action takes place. The results obtained in the following experiment were also unexpected.

EXPERIMENT V.

Take equal pieces of soft zinc, copper, iron, or brass, beat one of each pair on a smooth anvil till they are as hard as possible. Form a binary combination with pairs of the same metal, and use diluted sulphuric acid, and it will be found by the galvanometer that the hard metal in each case corresponds with zinc in the standard battery. If two pieces of steel be employed, one of them soft, and the other tempered, a galvanic effect will be produced, but of a contrary character. The soft steel will correspond with zinc, and the hard with copper, in the battery of comparison. The result of the following experiment seems also at variance with previous notions on the subject.

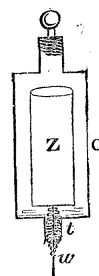
EXPERIMENT VI.

Having procured two small iron bars, with the ends made bright with a file, and copper wires connected with the other ends, I heated the end of one of

them, connected the wires with the galvanometer, and then immersed the hot and cold ends in water; a considerable action took place, and the cold iron was found to correspond with zinc in the standard battery. Since oxygen combines more rapidly with hot than with cold iron, positive electricity ought, according to the received opinions, to have appeared at the hot iron, whereas the contrary was actually the case. The following experiment is not only at variance with the theory of Dr. WOLLASTON, but seems also hostile to some of the generally received notions of chemists.

EXPERIMENT VII.

Let C be a cylinder of copper, about an inch in diameter, and two inches long, having a small copper tube *t* soldered in one end, whilst the other end is left open. Let Z be a small cylinder of zinc, having a copper wire *w* soldered to the lower end. The wire, being covered with a thread and passed through the tube, is firmly cemented with electric cement, metallic contact being carefully avoided. Another end having a strong brass tube with an internal screw is now soldered in the top of the copper cylinder. The interior surface of the cylinder of zinc is covered with electric cement to prevent the acid acting on it. The whole is now nearly filled with water, and a little sulphuric acid is introduced into the zinc cylinder by means of a very slender glass funnel. The whole is now completely filled with water, and a solid screw dipped in electric cement, and screwed into the top of the brass tube, whilst it is heated, renders the whole completely air-tight. The acid is now to be mixed with the water by frequently inverting and shaking the cylinder. If the copper and zinc cylinders be connected with the galvanometer, the battery will continue to act for a day or two with the same energy as if the whole had been left exposed to the air. As there is no room for the disengagement of hydrogen, the oxygen of the water cannot combine with the zinc to convert it into an oxide; nevertheless chemical action goes on, and the zinc is dissolved in the acid. From this experiment it is obvious that the oxidation of the zinc and the combination of nascent hydrogen with the electric fluid, as Dr. BOSTOCK supposes, has nothing to do with the production or transfer of the electricity which appears at the surface of the zinc. The metal is still, however, dissolved or reduced from



a solid to a fluid state ; and as its capacity for caloric has undergone a change, may not its capacity for the electric fluid have also undergone a certain change? Hence it is possible that the true theory of galvanism may be more intimately connected with that of latent heat than has yet been supposed. Since the zinc is dissolved without the assistance of oxygen from the water, it appears that the atoms of the acid have combined with the pure brilliant atoms of the metal, without the necessity of the metal being first converted to an oxide.

From the short view that I have taken of this interesting subject, it appears that the electric theory is quite unfounded, and that the chemical theory will require some modification to embrace the facts contained in the last experiments. This I shall not, however, attempt at present ; as my object in this paper is rather to demolish old fabrics and collect new materials, from which a more substantial edifice may be raised.