

Valeria Mosini

When Chemistry Entered the Pile

1. Introduction

In March 1800 Volta wrote to Sir Joseph Banks describing an apparatus he had just invented, asking Sir Joseph to communicate the new results to the Royal Society. The apparatus in question produced shocks, sparks and a continuous current; the apparatus was arranged either as a “crown of cups” or as a “pile” of bimetallic elements.¹ Volta compared it to the natural electric organ of fish like the torpedo, and attributed its electromotive force to the different affinity for electricity of the metals used as electrodes. Testing Volta’s apparatus, William Nicholson and Antony Carlisle carried out the-admittedly-unplanned first electric decomposition of water, leading to the extrication of hydrogen and oxygen from two distinct points. The effect of Nicholson and Carlisle’s experiment on the scientific community was “as electric as the discovery behind it”² and, on Humphry Davy’s account, the experiment represented “the true origin of all that has been done in electrochemical science”.³ Notably, the experiment contained elements that favoured Fabbroni’s thesis (1799) that chemical, rather than electrical, effects caused galvanic phenomena. Among them the observations that an acid was produced, that the bulk of the copper electrode increased ten times, and that brass, gold and platinum, used as electrodes, brought about different results.

Volta congratulated Nicholson on the experiment, but, nonetheless, continued to claim that the current in the pile resulted from the different affinity for electricity of silver and zinc: on his account, the chemical effects occurring in the apparatus were a mere consequence of the electric current produced by it. Volta’s refusal to admit that the chemical theory provided a credible alternative to his contact theory of metallic electricity in the explanation of galvanic phenomena flew in the face of much of the evidence gathered in the first years of the 19th century. Among the possible explanations of his attitude is the fact that, having his contact theory been

¹ *VO*, II, pp. 5-11.

² LILLEY (1948), p. 84.

³ DAVY (1826), p. 383.

accepted against Galvani's, he was not prepared to concede that other theories, for instance, Fabbroni's, could explain galvanic phenomena. Moreover, being the inventor of the pile, Volta was fully entitled to assume he had understood the mechanism underlying it. The esteem and admiration that the scientific community tributed him, expressed in the prize awarded by the Royal Society, and in Napoleon's gold medal, did little to change his habit of being "seldom influenced by the work of others, except at the beginning of an investigation".⁴ A habit that resulted in an attitude to scientific matters that was stubborn⁵ and arrogant.⁶

Volta's disregard for the role of chemical phenomena in the functioning of the pile has been rightly noted and discussed.⁷ However, as I claim in this paper, focusing on it⁸ may lead to wrong conclusions. Such as that the contact theory and the chemical theory provided rival explanations of the functioning of the pile, i.e. that a controversy existed, in which Volta took sides. In fact, at the beginning of the nineteenth century, neither the theory of electricity nor that of chemical reactivity had a sufficiently developed theoretical framework, let alone a fully specified ontology. The relation between the chemical theory and the contact theory cannot be construed as a controversy: these theories represented nothing more than plausible hypotheses in explaining the functioning of the pile. Rather than criticising Volta for failing to appreciate the role of chemical phenomena in the pile, I wish to praise his early recognition of the inextricable link between chemical and electrical phenomena.

To discuss Volta's attitude to the role of electrical and chemical phenomena in the pile, it is useful to summarise the main steps of the investigations that led to the epoch-making invention.

2. From Animal Convulsions to the Pile

Investigations carried out by Galvani between 1791 and 1792 showed that connecting the nerves and muscles of animals by means of a bimetallic arc resulted in muscular contractions in the animals' limbs. Galvani interpreted his findings as proof of the existence of animal electricity, and equated the effect of joining the animal's muscles with the nerves with the discharge of a Leyden jar. Initially Volta was very impressed with Galvani's findings and described them as "a major discovery, an epoch-making one, not so much in itself but for the theoretical and practical possibilities it opens up".⁹ He thought that animal electricity resulted from the nerves being charged negatively, the muscles positively, and that the function of

⁴ HEILBRON (1976), p. 80.

⁵ HEILBRON (1977).

⁶ PERA (1992).

⁷ WHITTAKER (1951); PARTINGTON (1964); HEILBRON (1977).

⁸ USSELMAN (1989).

⁹ *VO*, I, p. 15.

the metallic arc was simply that of bringing to equilibrium the state of the animal by transferring the electric fluid from the nerves to the muscles.¹⁰

The investigations performed over the summer of 1792, however, led Volta to conclude that there could be no electricity imbalance between muscles and nerves since these organs and the surrounding tissues are conductors of electricity. He also noted that the hypothesis of animal electricity could not explain why some metals produced stronger contractions than others in the animal's limbs. One experiment in particular contributed to Volta's change of mind. It showed that the connection of two different metals through a third metal, could, in the absence of animal organs, generate electric shocks.¹¹ He concluded that metallic, not animal, electricity was the cause of the phenomena that Galvani had observed, and claimed that "the metals used in the experiments, when applied to the moist bodies of animals, can by themselves, and of their proper virtue, excite and dislodge the electric fluid from its state of rest; so that the organs of the animal act only passively".¹² This was the starting point for Volta's "special contact theory"; it described metals not just as conductors but as motors of electricity, albeit, each one at its own degree,¹³ and attributed a role, that of transferring the electric fluid from one metal to the other, to the moist conductors. Notably, he only provided tentative suggestions as to the action of the moist conductors.¹⁴

When Galvani showed that animals' limbs contracted even by connecting nerves to muscles with a non-metallic body or with a single metal, Volta modified his theory and generalized the power of generating electricity from metals to moist conductors.¹⁵ He stated that the simple juxtaposition of three different conductors, whether two metals and a moist conductor, or two moist conductors and a metal, or three moist conductors, was sufficient to generate an electromotive force. Volta conceded that he was not yet in a position to explain "the manner" in which metallic electricity originated, but, nonetheless, urged that its existence should be accepted as an undeniable fact.¹⁶ He was convinced that the quantitative measure of an effect was precondition to ascertaining its nature and origin: "How can causes be found if one does not determine the quantity as well as the quality of the effects?".¹⁷ Hence he saw the low intensity of metallic electricity, which prevented quantitative measurements even with the most sensitive electrometers available at the time, as a major obstacle to explain the mechanism behind it. With the introduction of

¹⁰ *Ibid.*, pp. 73-7.

¹¹ *Ibid.*, pp. 43-74.

¹² *Ibid.*, pp. 173-98.

¹³ *Ibid.*, pp.133-41.

¹⁴ *Ibid.*, pp.113-8.

¹⁵ *Ibid.*, pp. 289-301.

¹⁶ *Ibid.*, pp. 417-31.

¹⁷ *Ibid.*, pp. 3-7.

Nicholson's doubler,¹⁸ and on a modified and improved version of Bennett's condensing electrometer, Volta was able to measure the intensity of the metallic electricity released by each couple of metals or moist conductors. On the basis of these measurements, he listed the metals according to the intensity of their electric effects,¹⁹ and this knowledge opened the way for the invention of the pile.

As is well known, Volta's contact theory was not the only alternative to animal electricity in the explanation of galvanic phenomena. Another Italian scientist, Giovanni Fabbroni, had noted that the presence of water was essential for galvanic phenomena to occur, and attributed the latter to chemical effects related to oxidation processes taking place in the solution.²⁰ In a paper read at the Accademia dei Georgofili in 1776, and published in 1779, Fabbroni reported several observations, all pointing in the same direction. For instance, he reported that, while isolated metals remained unaltered for a long time, two different metals brought in contact caused the oxidation of one metal. He explained this observation by claiming that the contact between different metals weakened the cohesion force between the molecules. In the presence of water, the altered molecular state established an attraction between the oxygen present in the water and the molecules of the metal that had weaker cohesion forces and, which, therefore, was oxidised. Fabbroni noted that the acid taste experienced by the tongue when touching different metals was much weaker if the tongue had been previously dried.²¹ These observations strongly suggested that oxygen played a role in galvanic phenomena, a suggestion further supported by another of Fabbroni's observations. This was that the oxidation produced when two different metals were put in contact in a vessel of water ceased if a film of oil or mercury was poured on the water surface, and that it could not be re-established by inserting a metal wire under the insulating layer. If, however, the water surface was covered with an oxygen-rich oxide, the oxidation of the metal occurred just as in the case in which the water surface was in contact with air. Consequently, Fabbroni attributed galvanic phenomena to chemical, rather than to electrical, effects.

One of the reasons why, despite the evidence that Fabbroni had provided, the scientific community of the time remained reluctant to endorse the chemical theory, was the suddenness with which the metals exerted their effects on the animal fibres. Fabbroni suggested that the surprise at this suddenness should be explained away on the basis of the consideration that "the chemical action exerts itself with the swiftness of lightning".²² He refused to rule out that electricity was involved in

¹⁸ NICHOLSON (1788).

¹⁹ *Ibid.*, pp. 289-301.

²⁰ It should be recalled that, in 1796, John Ash had investigated the behaviour of different metals brought together in the presence of water and concluded that one of the two was oxidized and that the greatest galvanic activity was associated with the greatest chemical activity.

²¹ See FABBRONI (1799), p. 121.

²² *Ibid.*

galvanic phenomena, and noted that chemical processes often resulted in an imbalance of electricity, and that, in turn, frictional electricity induced chemical action. He wanted to avoid discussion on the possible relationship between electrical and chemical phenomena on the grounds that electricity was, in his eyes, “un agent presque inconnu”,²³ not to be treated on a par with the chemical agents on which he felt fully competent.

Fabroni’s views found a receptive audience in Germany, notably in the case of Ackermann, Ritter, and Reinhold, among others. Humboldt (1799) postulated a connection between galvanic and chemical phenomena but attributed its origin to physiological processes occurring in the animal’s body. In line with Fabroni, he believed it premature to locate the origin of galvanism in electric phenomena when so little was known about electricity.

3. Chemical Phenomena and Electric Current

Volta’s letter to Sir Joseph aimed to promote a reaction to the invention of the pile from the British scientists, particularly from Cavallo, Bennet, and Nicholson,²⁴ all of whom had given outstanding contributions to the field of electricity.²⁵ Among the three scientists, Volta was addressing Nicholson in particular. This is because Nicholson had carried out investigations on the electric organ of the Torpedo fish and explained its functioning through a conjecture that Volta had praised as “the most probable that the existing theory of electricity could at that time afford”.²⁶ Moreover, three years before the invention of the pile, Nicholson had predicted the invention of a machine “capable of giving numberless shocks at pleasure, and of retaining its power for months, years, or to an extent of time of which the limits be determined only by experiment”.²⁷ Not too surprisingly, his investigations on Volta’s invention turned out to promote utterly unexpected developments, which included a serious challenge to the contact theory in the explanation of the functioning of the pile. Here are Nicholson’s experiments in some detail.

Initially, Nicholson collaborated with his friend Antony Carlisle, resident surgeon at Westminster Hospital, who was also a personal friend of Sir Joseph’s.

²³ FABBRONI (1799a), p. 348.

²⁴ See VO, I, pp. 5-11.

²⁵ Recall that Cavallo and Bennet had published two of the most influential textbooks on electricity, *A Complete Treatise of Electricity* (1777) and *New Experiments on Electricity* (1789) (see LILLEY (1948), p. 84) and that, in 1797, Nicholson had founded the *Journal of Natural Philosophy, Chemistry, and the Arts*, the first scientific periodical in English to be published independently of the Academies (*ibid.*).

²⁶ VO, I, p. 15.

²⁷ NICHOLSON (1797), p. 358.

It was Carlisle who suggested a slight modification in Volta's standard apparatus, a modification that was going to bring about the unplanned electrolysis of water. Carlisle suggested adding a drop of water to the contact of the upper plate of the pile to make it more secure. As the pile was set in operation, a small quantity of gas evolved from the water placed on the touching wire.²⁸ The production of gas, though in minute quantity, appeared to Nicholson and Carlisle remarkable enough to be investigated further. With this aim, they did an experiment in which the brass wires applied to the extreme end of a pile of 36 half crowns and 36 pieces of copper with pieces of wet cardboard interposed were inserted in two corks placed on top of a glass tube filled with water. A fine stream of minute bubbles immediately developed around the wire connected with the silver end while the wire connected with the zinc end became tarnished, deep orange, then black. Reversing the connections between the wires and the extremity plates of the pile reversed the effects observed, which were restored as at the beginning of the experiment by reversing the connections again. After the pile had functioned for 2 1/2 hours, the upper wire started to emit "clouds" of an unknown substance which, towards the end of the experiment, became of a pea green colour, and, landing on the lower extremity of the tube, made the water semi-opaque. The gas, produced in the quantity of 2/30 of a cubic inch, and mixed with an equal amount of common air, exploded upon application of a lit waxed thread.

The authors noted that the decomposition of water increased as the distance between the wires decreased, but ceased if the wires were put in direct contact. They noted that the decomposition of water was not in itself unexpected: "We had been led by our reasoning on the first appearance of hydrogen to expect a decomposition of water".²⁹ However, they noted that "it was with no little surprise that we found the hydrogen extricated at the contact with one wire, while the oxygen fixed itself in combination with the other wire at the distance of almost 2 inches. This new fact still remains to be explained, and it seems to point at some general law of the agency of electricity in chemical operations".³⁰

A few days after the first experiment, Carlisle tested again the pile replacing the brass wires with copper wires, and adding litmus tincture to the water. In about ten minutes, the solution turned red around the oxidating pole, remaining blue around the negative pole. Nicholson's comment was the following: "it seems either an acid was formed, or that a portion of the oxygen combined with

²⁸ See NICHOLSON (1800).

²⁹ *Ibid.*, p. 183.

³⁰ *Ibid.*

the litmus, so as to produce the effect of an acid”.³¹ Moreover, he noted that adding common salt to the water resulted in an efflorescence of soda at the ends of the pile. To investigate whether the metallic surface in contact with water was in any way related to the intensity of the shock produced by the pile or to the degree of decomposition of water, Nicholson constructed a “small pile” operated according to the standard procedure.

The small pile consisted of two piles of 16 disks of silver alternated with disks of zinc and wet cardboard. The disks were 2 and 1.8 inch in diameter, those of silver were as thin as one thousandth of an inch, while those of zinc were the twenty-fourth part of an inch. The experiment showed that neither the surface nor the thickness of the plates added to the force of the pile. As to the nature of the gases given off, Nicholson inferred that hydrogen was released at the silver end, oxygen at the zinc end.

The decomposition of water and the oxidation of the metallic wires gave rise to a variety of speculations and projects of experiments. One such project concerned the elucidation of the behaviour of metals of difficult oxidation like platinum and gold. Replacing the brass wires with platinum or gold wires, Nicholson noticed that the silver end gave off almost as plentiful a stream of gas bubbles as the zinc end. The water did not appear semi-opaque, as it had in the previous experiment. Moreover, no signs of oxidation or tarnish appeared after the pile had functioned for over four hours. Replacing one platinum or gold wire with brass gave rise to different results depending on which end had been replaced. When the brass wire was on the negative side, two gases were produced, as in the experiment with two gold wires, and no signs of oxidation appeared. But when the brass wire was on the positive side, it became oxydised, as it was when both wires were made of brass. Another experiment, in which both wires were gold and the process was carried out for a long time, showed that the wire in contact with the zinc acquired a “coppery tinge”. However, it was impossible to ascertain “whether this arose from oxidation of the gold or of the copper contained in the gold in a quantity of about a seventieth part”.³² As to the last experiment reported in the paper, Nicholson described it as “the most remarkable of those which I have yet observed”.³³ It consisted in a pile constructed as usual but having pieces of wet woollen cloth instead of wet cardboard gave severe shocks and produced large quantities of gases. When copper wires were used for the broken circuit and muriatic acid diluted with 100 parts of water replaced pure water, there was no production of gas if the distance

³¹ *Ibid.*

³² *Ibid.*, p. 185.

³³ *Ibid.*, p. 186.

between the wires was 2 inches. If the wires were at the distance of 1/3 of an inch, hydrogen was given off at the minus pole while the other pole was corroded. When the pile had been operating for four hours, the bulk of the copper wire on the minus side became nine or ten times bigger than it was initially, at which Nicholson concluded: “we are in want of a measure of the power of these machines”.³⁴

Volta praised Nicholson and Carlisle’s experiments, and claimed that he had been very close to carrying them out himself. He conceded that the oxidation of the metals which, as Nicholson had shown, accompanied the electrolysis of water, was to be considered “not just an extraordinary thing, but a thought-provoking one”.³⁵ However, he attributed it to the weak and continuous current produced by the apparatus.³⁶

The publication of Nicholson and Carlisle’s findings prompted research aimed to improve the understanding of the functioning of the pile. In France, Volta’s contact theory received support when, in 1801, Guyton operated piles in which the fluids were replaced with salts and starch powder. In England, in fact, things took a different turn. Nicholson’s *Journal* had become the main forum for discussion on galvanism with the publication of over one hundred papers in the first years of the nineteenth century.³⁷ Davy gave important contributions to the discussion, for instance, by showing that the current flow of a pile was zero if pure water was used as the fluid interposed between the metals.³⁸ Among his observations was the fact that a pile in which electrodes of the same metal were put in contact with different fluids was equivalent to Volta’s pile. He also showed that an exhausted pile could be recharged simply adding to the fluids small quantities of concentrated solutions of the proper chemical agents.³⁹ Lastly, Davy disproved Guyton’s theory that moist conductors could be replaced by solid substances (for instance, that a copper/zinc pile could be operative with dried starch powder interposed between the metals) by showing that, for the pile to work, the solid substance must have absorbed some water.⁴⁰ Cruickshank reported that metals precipitated at the electrodes from saline solutions,⁴¹ and Haldane that the production of an electric current in the pile critically depended

³⁴ *Ibid.*, p. 187.

³⁵ *VO*, I, p. 6 (my translation).

³⁶ *Ibid.*

³⁷ See LILLEY (1948).

³⁸ See DAVY (1800).

³⁹ See DAVY (1801).

⁴⁰ See DAVY (1802).

⁴¹ See CRUICKSHANK (1800).

upon the oxidation of the zinc.⁴² Summing up, the gist of the papers published in Nicholson's Journal at the beginning of the nineteenth century was one and the same: that the substances dissolved in the fluids played a crucial role in the functioning of the pile.

Yet, notwithstanding the evidence gathered by the British scientists, Volta continued to claim that the chemical effects taking place in the pile were a mere consequence of the electric current running through it:

ce n'est pas que l'action galvanique, qu'on doit reconnoitre enfin n'être autre chose qu'une action proprement électrique, s'exerce ni en tout, ni principalement par l'attouchement de l'humide avec le métal; ce n'est pas non plus, que cette action réponde à l'action chimique, que tel ou tel liquide a sur tel ou tel métal, à l'oxidation du métal, etc., comme plusieurs s'étoient imaginé.⁴³

Accordingly, he explained the observation that saline solutions, used instead of water, increase the power of the pile, by invoking their better conducting power with respect to pure water.

4. Electricity and Chemistry at the End of the Eighteenth Century

Volta's disregard for the role of chemical phenomena within the pile has been repeatedly pointed out in recent times (see, for instance, Whittaker,⁴⁴ Usselman,⁴⁵ and Partington⁴⁶). By contrast, the scientists of Volta's time only mentioned it in passing. Nicholson, for instance avowed that he could not "look back without some surprise, and observe that the chemical phenomena of galvanism, which had much been insisted upon by Fabbroni, more especially the rapid oxidation of the zinc, should constitute no part of Volta's numerous observations".⁴⁷ He blamed Volta's position, largely endorsed by the French scientists, on the poor circulation of his Journal in Europe. On his account, this caused "those very learned men to be too precipitate in admitting the electric energy as the only effective agent in the phenomena of the pile, and that the fluids act merely as conductors".⁴⁸ In 1800, reviewing the evidence on the mechanism at work in the pile, Davy only remarked that "it seems reasonable to conclude, though with our present quantity of facts we are unable to explain the exact mode of operation, that the oxidation of the zinc in

⁴² See HALDANE (1800).

⁴³ VOLTA (1801), p. 91.

⁴⁴ WHITTAKER (1951).

⁴⁵ USSELMAN (1989).

⁴⁶ PARTINGTON (1964).

⁴⁷ NICHOLSON (1800), p.181.

⁴⁸ NICHOLSON(1802), p. 142.