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Debating the Nature of Voltaic Electricity, 1800-1850

The invention of Volta's pile started a long lasting controversy on the nature of voltaic electricity, the overview of which is provided by Helge Kragh in volume 1 of *Nuova Voltiana*.[1] In particular, he indicates that the controversy subsided in the 1840s and rekindled in the 1880s with a new focus on the nature of contact potential. This change of subject implies that it may be possible, if not necessary, to discuss separately the earlier period, when the controversy still revolved around the original question: does the electricity produced in a voltaic circuit originate from the mutual contact of two different metals or from chemical reactions? Yet, even within this earlier period, the amount of material available and the number of relevant issues to be addressed preclude a comprehensive coverage within the space limitation of this paper. Thus, I will bring up only a few questions, illustrating them by selected examples. The focus will be on interaction between theory and experiment and on a certain way of resolving a theoretical dispute.

1. Background

Formally, the controversy in question began in 1800 with the publication of the paper "On the Electricity excited by the mere Contact of conducting Substances of different Kinds" by Alessandro Volta (1745-1827), professor of physics at the University of Pavia. The first part of the paper was submitted to the Royal Society of London in the spring of 1800, and the full paper was read before the Society on June 26.[2] The paper described a new apparatus, that became known as the "voltaic pile," which was able to affect an electrometer and excite the sensations of shock, taste, light, and sound.

The apparatus consisted of many pairs of different metals, such as silver and zinc or copper and zinc, separated from one another with pure or salt water. In one form

[1] KRAGH (2000).
[2] VOLTA (1800); also in VOLTA (1800a); English translation in VOLTA (1800b), republished in VOLTA (1800c).

of this apparatus (the "pile") all these couples made up a column arranged from the bottom up, for instance, as follows: copper, zinc, wet cardboard, copper, zinc, wet cardboard, etc. Another version, (the "chain of cups") consisted of a number of non-metal cups filled with salt water, each of which contained a pair of zinc and copper plates partially immersed into the liquid. The cups were arranged so that the zinc of one cup was electrically connected to the copper of another cup, and so on. Volta maintained that the electricity produced originates in the contact of different metals, with the liquid being merely a conductor.

Several English scientists who had seen the first part of Volta's paper before it was read at the Royal Society, constructed voltaic piles and began experimenting with them. In addition to the effects described by Volta, they found that a pile can produce various chemical phenomena. In particular, Anthony Carlisle and William Nicholson observed the release of oxygen and hydrogen, which they attributed to decomposition of water, and also an oxidation of metals, while William Cruickshank precipitated a number of metals. A few months later, on the basis of these and other experiments, William Hyde Wollaston (1766-1828) and Humphry Davy (1778-1829) suggested that, contrary to Volta's opinion, liquids must play an active role in galvanic phenomena, and Wollaston went as far as to state that chemical reactions may be the cause of electricity rather than its consequence.[3] Since in the ensuing exchange Volta argued that he had proved his theory prior to 1800, we have to look into its origin and the evidence supporting it.

Volta's theory appeared in 1792 as an alternative to the theory of "animal electricity" that Luigi Galvani (1737-1798), professor of anatomy and obstetrics in Bologna, offered to account for the phenomenon he had published in 1791. Galvani observed that when he connected the sciatic nerve and the leg of a prepared frog with a metal arc, usually made of two different metals, the leg twitched.[4] He concluded from his investigations that the agent responsible for this effect must be electricity, and since no known kind of electricity appeared to be involved, he suggested that it was the "animal electricity" long sought for by physiologists. Somehow an imbalance of electricity was created between nerves and muscles in an animal body, as in a Leyden jar, and connecting them with a metal arc produced an electrical "discharge" that stimulated the contractions.[5]

Volta agreed that the phenomenon was electrical but he assumed the main source of electricity to be outside the frog, in the contact of the metals of the arc with the animal tissues. In Volta's view, a metal attracted electricity from a wet substance, of the two only the metal playing an active role. Due to their different capacity for this attraction, different metals placed in contact with wet substances, such as the nerve and the muscles, accumulated unequal "amounts" of electricity (in modern terms,

[3] WOLLASTON (1801).
[4] GALVANI (1791).
[5] KIPNIS (1987); PERA (1992); BERNARDI (2000).

unequal potentials). As a result, when different metals came into contact, the imbalance of electricity created a force capable of moving electricity ("electromotive force"). That was what Volta meant by calling a contact of two metals an "electromotor". Since this theory could not explain the convulsions produced with a single metal, Volta maintained for a while both his contact electricity and Galvani's animal electricity.[6] Then in 1794 he discovered experimentally that a difference in temperature or polish at the ends of a wire was sufficient to excite contractions. Thus, he concluded, contact electricity alone was sufficient to explain all the phenomena, since a single wire with heterogeneous ends could be considered as two different metals. Giovanni Aldini (1762-1834), professor of physics at the University of Bologna and Galvani's nephew, countered this argument with a new experiment. He showed that mercury free of the heterogeneity described by Volta produced contractions, and so did charcoal. Another strong blow to Volta's theory came from Galvani's experiment in which contractions occurred when a nerve directly touched the muscle without any intermediaries.

First, Volta tried to find a flaw in his opponents experiments, such as mechanical pressure or a chemical difference at the ends of the connecting arc, but eventually he decided to modify his own theory. Prior to that, he concluded from his experiments that the simplest circuits to create contact electricity consisted of two different conductors of the first class (metals and some other solids) and one conductor of the second class (liquid or a humid body), or of two different conductors of the second class and one of the first class. In these circuits, the mover of electricity ("electromotor") was the contact of two different metals or the contact of a metal and a liquid. In 1795, Volta added to these two kinds of circuits a third variety made of three different conductors of the second class.[7] This modification was specifically designed to explain the "all-animal circuit", in which the conductors in question were the nerve, the muscles, and the animal fluids of the frog. Thus, in the new theory, which is called here the "universal contact", the contact of *any* two different substances was an electromotor.

The role of a humid conductor had always been a problem. Initially, Volta assumed that metals can attract electricity from water and other liquids. Later on, having experimented with various combinations of the conductors of the first and second classes, Volta found that the circuits where metals had wet conductors on both sides of them did not work. He was still uncertain, however, whether the moving force originated at the contact of two different metals or of a metal and a humid substance.[8] Eventually, he decided that the contact of two metals was the strongest electromotor, that of a metal and a liquid was much weaker, and that of two wet substances was even weaker. The evidence for that came from experiments with a frog: bimetals produced

[6] VOLTA (1793), p. 207; also VOLTA (1793a).
[7] VOLTA (1795); VOLTA (1796), p. 417; also VOLTA (1796a).
[8] *VO*, I, pp. 230-2.

the strongest contractions, a single metal excited only slight contractions, while convulsions in the "all-animal" circuits occurred only in very sensitive frogs.

Although Volta's theory of universal contact explained all galvanic phenomena, this generality was achieved at a heavy price: it drastically reduced the theory's heuristic and demonstrative capabilities. For instance, Volta's statement that any three conductors of the second class created contact electricity could not be independently verified, for the only experiment supporting it – the "all-animal circuit" – was the one that the hypothesis was created to account for. Actually, his knowledge that the contractions produced by conductors of the second class were much weaker than those by two different metals and a liquid opened a path for returning to his original theory that the weakest contractions may result from internal animal electricity while the stronger ones come from external electricity. Volta, however, chose not to do that, and it took about fifty years until such a theory began to gain strength.

By 1795, Volta realized that he could not fully establish the existence of contact electricity without eliminating the animal electricity. The main difficulty with this was that a prepared frog was the only available sensitive detector of galvanic electricity: one could always say that the electricity responsible for muscular contractions came from the frog itself rather than from the external part of the circuit. For this reason both theories had about the same standing among scientists. The only way to prove that electricity was created by a contact of different substances was to replace a frog by a non-animal electric sensor, and Volta decided to try Nicholson's doubler of electricity.[9] He placed silver and tin rods on a wet piece of cardboard, brought them into contact with the two brass discs of the doubler and started the "machine": after 20-30 turns, the leaves of the electrometer diverged by 6 to 10 degrees. When he replaced the brass mobile disc with the tin disc and connected it to a brass rod while a brass disc touched a tin rod, the doubler showed a noticeable quantity of positive electricity. However, when he reversed the connections, having each bar touching the disc of the same metal, there was no sign of electricity. Volta interpreted this result as a proof that electricity is created at the junction of dissimilar metals rather than at the junction of a metal and a liquid.[10]

While Volta was convinced that he found the decisive proof of the existence of contact electricity, other scientists were not so enthusiastic about it. The doubler was known for producing "spontaneous" electricity that was difficult to get rid of, which implied that while multiplying an extremely weak "signal" the instrument might have added to it an uncertain amount of "noise." Consequently, this experiment did not produce on the scientific community the effect Volta had expected. Galvani died in 1798 unconvinced, and Aldini continued to fight for his theory for many years to come. Volta was disappointed by such resistance, for he considered his case clear and free of any flaws, because his theory of "universal contact" covered everything.

[9] VOLTA (1797).
[10] VOLTA (1796).

Apparently, he saw no difficulty with the new experiment of Galvani in which contractions occurred when the nerves of two frogs touched one another.[11] While to Galvani two nerves were similar substances, no one could prevent Volta from treating the nerves of different frogs as dissimilar. Without a rigorous definition of "similarity" or "homogeneity" Volta could have applied this concept any way he wanted.

Regardless of its success in the debate with Galvani, the theory of contact electricity led Volta to one of the greatest discoveries of the nineteenth century: the electric pile.

2. The Pile

The discovery was made at the end of 1799, and it became first known through Volta's paper in the *Philosophical Transactions*. The paper begins with a promise to inform of "some striking results I have obtained in pursuing my experiments on electricity excited by the mere mutual contact of different kinds of metal, and even by that of other conductors, also different from each other, either liquid or containing some liquid, to which they are properly indebted for their conducting power".[12] This sentence, as well as the title itself, already contains a complete theory of the apparatus to be described. By offering a theory up-front, Volta implies that the purpose of the paper is not so much to get additional support for this theory as to describe some remarkable phenomena he observed by means of a new apparatus.

This device consisted of many similar components, each of which included two different metals ("couples"), such as silver and zinc or copper and zinc, and a piece of cardboard or cloth moistened with pure or salt water. In one form of this apparatus (the "pile") all these components made up a column arranged from the bottom up, for instance, as follows: copper, zinc, cloth, copper, zinc, cloth, etc. Another version of the apparatus (the "chain of cups") consisted of a number of non-metal cups filled with salt water, each having a zinc and a copper plate immersed in water. The cups were arranged so that the zinc of one cup was connected to the copper of another cup, and so on.

Volta observed that when the number of couples was sufficiently high, the pile produced a shock similar to that of a Leyden jar. In addition to a shock, the apparatus could affect an electrometer and produce an electric spark, although these actions were less pronounced than the shock. For these reasons, Volta compared his apparatus (it became known as the "voltaic pile") to a battery of Leyden jars, "weakly charged" but of an "immense capacity". However, he emphasized two important differences between them: 1) a pile acts continuously, providing repeated shocks without being recharged by external electricity, 2) it consists solely of conductors of electricity. Volta drew two consequences from this difference. One is that this is the first "perpetual" source of electricity. Another one, less known, is an

[11] PERA (1992), p. 147.
[12] VOLTA (1800a), p. 565.

explanation of the electric torpedo.

While in Volta's view, he had already refuted the "frog's electricity" in 1797, the electric fish still remained a mystery. In fact, Volta never doubted that the shock produced by the torpedo was electrical, nor did he question that the electricity involved, unlike the case with frogs, resides inside the animal. His main argument with physiologists was that if electricity had any role in animal life, it could be explained by physical factors alone without bringing in any mysterious "vital forces". As for frogs, he had already demonstrated – or so he believed – that their contractions were due to external contact electricity. In the case of the torpedo, however, his task was different: to conceive a physical model of its electric organ. Without fulfilling this task, Volta did not feel that his program of explaining life phenomena by physical processes was complete.

Volta began with a critique of William Nicholson's theory of the electric organ of the torpedo, which compared it to a battery of Leyden jars. In Volta's view, since all membranes making up the columns of the electric organ are filled with fluids, they are comparatively good conductors. Since a Leyden jar cannot be made without an insulator, Volta concluded that the electricity produced by the torpedo and some other fish could not be static electricity. On the other hand, his pile consisted solely of conductors, and this, Volta supposed, could be the necessary model: the electricity of fish was galvanic, being produced by the contact of organic substances of different nature. To support this theory he indicated that his apparatus produced shocks comparable in strength to those of a languid torpedo, and that it could give repeated shocks. He even called his apparatus an "artificial electric organ". This name and the initial shape of the apparatus – a column – showed that an explanation of the electric organ of the torpedo was an essential, if not the most essential, goal of this paper.[13]

Volta maintained that only a junction of two metals was an electromotor, while the liquid itself was only a conductor. Since one of the two metals attracted electricity more strongly than the other, each couple moved the electricity in a certain direction, e.g. from zinc to copper. Thus, if several couples had the same orientation, their efforts combined, and the electricity moved faster: the more couples, the better.

Although Volta insisted that he did not need the pile to support his theory of contact electricity, it was the pile that made many scientists turn to Volta's theory from that of Galvani. They reasoned as follows: 1) the actions of the pile are electrical, 2) since its effect is nothing but a multiplied effect of a single couple, a

[13] A. Mauro reduces Volta's theory to that of metal contact and thus concludes that a voltaic pile could not be a proper model of the torpedo, because animal tissues do not contain any metals. See MAURO (1968). Joost Mertens committed another error when interpreting the shock experiments as aiming at convincing, by means of amusing experiments, a wider audience rather than experts. In particular, he sees a sign of showmanship in Volta's recommendation to immerse the whole hand into water, while, in fact, this device, compared to immersing a finger, serves merely to reduce the resistance of the circuit, which is essential when the number of couples in the pile is comparatively low. See MERTENS (1998).

contact of two different metals creates electricity too, 3) the electricity created by a bimetal is the same whether it is detected by an electrometer or by a frog, thus Galvani's experiments were due to contact electricity rather than animal electricity. In fact, the last conclusion was not logical, since a circuit with a frog could have had both sources of electricity, but this detail went unnoticed.[14] Likewise, few people noticed that they had begun using the term "galvanic" ("galvanic circuit", "galvanic current", etc.) to refer to phenomena produced by a voltaic pile rather than to those involving frogs. Yet, while securing Volta's victory over animal electricity, the pile brought to life an even more powerful rival, the chemical theory.

3. The Early Debate

The chemical theory was initiated by Giovanni Fabbroni in 1792, but it became known only after 1797. According to Fabbroni, the primary cause of galvanic phenomena was chemical reactions rather than electricity. The basis for this theory was provided by the inability of electric theories to explain certain phenomena, in particular, the existence of contractions with the circuit open, or a prolongation of the sensation of taste after the removal of the bimetal. Fabbroni experimented with different metals immersed in water and found that one of them oxidized, but only if the metals touched one another on the outside. This observation led him to suggest that the galvanic phenomena are due to oxidation. Fabbroni did not try to eliminate electricity from galvanic phenomena altogether, rather he insisted that chemistry must have some role in them, in particular, in producing the sensations of taste or light.

The first chemical theory had a number of followers, including Alexander von Humboldt, and it was limited to galvanic phenomena in the original meaning of this word. After the discovery of the electric pile, "galvanic phenomena" usually referred to physical-chemical phenomena involving a pile, and, accordingly, the chemical theory changed its focus, aiming to explain the origin of the electricity producing these phenomena.

Davy argued that the liquid plays an active role because in an iron-copper pile with water the iron is charged positively, but if water is replaced with sulfate of potassium the iron changes its electrification to negative.[15] He also created a pile using a single metal and two different liquids, an acid and an alkaline, the liquids in different cells being connected by paper strips moistened with water.

In his first responses to this criticism, Volta insisted that he had already proven the contact of different metals to be an "electromotor." He described an experiment in which he held a zinc plate and a copper one by insulating handles, touched them one to another, separated and brought them into contact with the plates of a condenser electrometer. The leaves of the electrometer diverged by 1 to 2 degrees.

[14] KIPNIS (1987), p. 135.
[15] DAVY (1800).

Since no third wet object was involved, Volta concluded that the electricity was produced by the mere contact of the two metals, without any chemical interaction. Then he measured the tension of a pile of 60 couples and, presuming that each couple contributed the same electromotive force and that all these forces added up in the pile, he concluded that the electromotive force created by a single couple was the same as that produced for the contact of copper and zinc plates. This means that the source of electricity in the pile is the contact of two different metals, while the liquid serves "no other purpose than to effect a mutual communication between all the metallic pairs".[16] As to the chemical effects observed in England, Volta called them "secondary effects" of voltaic electricity. Although he found that adding to water salt or an acid increased the effect of a shock, still he claimed that this was merely the result of improved conductivity, while there was no increase in the "electric force" as measured by an electrometer.

Nicholson, who translated and published this paper, was not satisfied with Volta's explanations and brought forth Davy's experiments as refuting Volta's theory.[17] Volta responded by referring to his experiments of 1794-98 as confirming his theory.[18] He asserted, in particular, that he was aware of an electromotive force created by a metal-liquid contact, which he found to be too weak compared to the one produced by two different metals. He noted, however, an exception: with alkaline solutions or concentrated acids the effect was quite noticeable. Volta also claimed to have carried out Davy's experiment with one metal and two different liquids, only in another form. Moreover, he added, since such a circuit was one of the active circuits permitted in Volta's theory, there was nothing new in Davy's experiments. Finally, Volta agreed to give chemical reactions some role, but only in improving the conductivity of the pile rather than in producing electricity: when an acid, for instance, attacks a metal surface, it adheres closer to it than water does and thus diminishes the resistance of this contact.[19]

The debate revealed several conflicts within Volta's theory, although its opponents did not always take advantage of them. One was that, depending on the method of estimating the "power of the pile" – a shock or an electrometer – one concluded that the choice of a liquid in a pile was, or was not important. As in static electricity, Volta took the deviation of an electrometer to measure the "tension" (or "intensity" of electricity), which he considered to be a measure of the "electromotive force". On the other hand, he treated the strength of a shock as a function of the "quantity of electricity", or, sometimes, of the "velocity of electricity".[20] In modern language, one method measures a difference of potential, the other, perhaps, an average current.

Although, the latter was not completely clear to Volta, he certainly understood

[16] VOLTA (1802), p. 138.
[17] NICHOLSON (1802).
[18] VOLTA (1802a).
[19] *Ibid*., p. 344.
[20] TEICHMANN (1977). See also his article in this volume.

that the two parameters in question were quite different, and using them according to his needs was one of his polemical tools. While on the offensive, Volta always argued that the chemical properties of a liquid were of no significance, referring to a constant tension shown by an electrometer. On the other hand, when pressed with evidence that the same pile filled with different liquids provided shocks of different strength, Volta tried to turn the shock method to his advantage too. He argued that different liquids changed the resistance of the circuit, which made a shock more or less powerful. The trouble with this argument was that Volta could not prove it, for, except for Cavendish's comparison of the conductivity of pure and sea water, no data for the conductivity of liquids existed not only for voltaic but even for static electricity. Fortunately for Volta, no one noticed this flaw.

It is worth noting that while the electrometer was his favorite method, because of its reliability and quantitative results, Volta could not have dispensed with shocks, because they supported his analogy between the pile and the torpedo. As a result, although it was less precise, according to Volta himself, this method dominated in his paper in the *Philosophical Transactions*.

The other conflict was between placing the seat of the electromotive force at different types of junctions. Before the invention of the pile, Volta maintained that any contact creates an electromotive force, which is the strongest at the contact of two metals, weaker at the contact of a metal and a liquid, and the weakest at the contact of two liquids or wet conductors. As long as he could neglect the electromotive force of a liquid-metal contact compared to that of two metals, which was the case in many of Volta's experiments, his theory did not suffer. However, in some cases in Volta's own experiments and in those of Davy mentioned above, the effect of a metal-liquid contact was comparable to that of a bimetal. However, Volta could not take the former into account when calculating the electromotive force of a pile: first, he did not know how to combine the two; and second, his electrometric measurements showed no influence of any electromotive forces different from that of the two metals.

While Volta did not know how to reconcile these contradictory features, he was certain that each of them was true and therefore must be retained. As a result of the inclusion of these contradictory features, Volta's theory became so flexible that it could counter any attack. For instance, if Volta wanted to emphasize the importance of the proper selection of a liquid, he referred to the shock experiment; but if he needed to demonstrate that the choice of the liquid was not essential, he pointed to the electrometer experiment. If he wanted to prove that the electromotive force of a pile was a product of metal-metal contacts, he invoked his 1797 electrometer experiment with two different metals; but to demonstrate his knowledge of the role of metal-liquid or liquid-liquid contacts, he referred opponents to his experiments with the prepared frog. While this way of discussion allowed Volta to win any argument, it created confusion about his true views even among his followers, who frequently tended to reduce his theory to that of a bimetal contact.

As early as 1802, Volta was able to convince the "chemists" that all their objections to his theory actually supported it, and this ended the first phase of the debate involving

Volta himself. The consensus was that chemically active liquids do play an important role in the pile, but it is impossible to prove whether this role is to produce electricity due to their reaction with metals, or to reduce the conductivity of the pile.

4. The Great Controversy

For the next two decades (1803-1823) Volta's theory appeared to be too firmly established to warrant extensive debate over an occasional criticism. I will mention only two examples of additional evidence to support Volta's theory, which are relevant for the subsequent discussion. In one, Biot confirmed by precise measurements – using a torsion balance – that the independence of the electromotive force of the selection of the liquid was a fact.[21] In another, Volta's theory received unexpected support from its former opponent, Davy. One of the strongest reasons for his conversion was his inability to find electricity associated with chemical reactions, the only exception being the contact of dry solid alkalis and acids. However, while Davy proclaimed himself a "contactist", his idea that the current in a voltaic circuit is a transfer of electricity brought new support to the chemical theory. Whatever the origin of the opposite electricities on zinc and copper plates, Davy said, its power would not support a current for more than a moment, if they were not constantly restored by oxygen and acids moving to zinc and alkalis and hydrogen to copper:

> The negative energy of the copper and the positive energy of the zinc are consequently again exerted [...] and the process of electromotion continues, as long as chemical changes are capable of being carried on. This theory in some measure *reconciles* the hypothetical principles of the action of the pile adopted by its illustrious inventor, with the opinions concerning the chemical origin of galvanism, supported by the greater number of the British philosophers.[22]

The word "reconciles" shows a new approach to the theory of the voltaic pile, which can be called the "compound" theory.

The new attack on Volta's theory began with the invention of an electromagnetic galvanometer in 1821. Some scientists believed that measuring current rather than tension could be a better method for finding connections between electricity and chemical affinity. Antoine-César Becquerel (1788-1878) was one of the first to begin working in this direction. His original purpose was to see if electricity is developed during a chemical recombination. He filled a platinum cup with an acid and held potash in platinum pincers, both the cup and the pincers being connected to a galvanometer by means of platinum wires to eliminate a metal-metal electromotive force. When potash touched the acid, the needle deviated showing that the acid was

[21] BIOT (1816), II, pp. 487, 528, 536.
[22] DAVY (1807), p. 46, italics added; also DAVY (1807a).

positive relative to the alkali.[23] Soon Becquerel realized, however, that he was not considering the contact effect between a metal and a liquid: following Volta, he thought of it as negligible.[24] Using a sensitive condenser electrometer, he began investigating whether a metal-liquid contact created a charge. A metal container with a liquid sat on the upper plate of the condenser, the lower plate being earthed. After touching the liquid with a finger and lifting the upper plate, he saw the electroscope showing the alkaline solution positive relative to the metal. On the other hand, an acid became negative relative to the metal. In another modification, the container was made of platinum, and so was the wire touching the lower plate, which eliminated the container-condenser electromotive force. The charges were the same as above. Not all metals gave perceptible charges, but when they did, in general, acids made metals positive, while bases made them negative.

Another proof of the active role of a liquid came from the following experiment. When a copper container filled with dilute acid sits on the upper plate of a condenser, touching the liquid with a hand-held zinc plate and simultaneously the lower plate with a finger made the copper container positive. Then Becquerel repeated the experiment with a zinc container filled with the same liquid: touching the lower plate with zinc (to eliminate the electromotive force of the condenser-container contact) and the liquid with a hand-held copper body made the zinc container negative. He concluded that when zinc and copper are separated by a solution, their polarity is opposite to the one acquired by direct contact.

Thus, while Becquerel began as a follower of Volta, he soon came to the conclusion that Volta's theory must be modified, in particular, that a metal-liquid contact was as important as a metal-metal one. Despite his inability to measure tension, he asserted that "it is thus almost certain that electromotive actions of conducting liquids on metals forming voltaic couples tend to augment the electric tensions of different elements of the pile".[25]

Gradually, Becquerel realized that the importance of a metal-liquid contact was due to a chemical reaction occurring there. He immersed one platinum wire from a galvanometer in nitric acid in a porcelain cup, while connecting the other wire to platinum pincers carrying gold wrapped in paper. No current appeared when the gold touched the acid, which, according to Becquerel, was expected, because the electromotive force of platinum was counterbalanced, and there was also no chemical reaction. Adding a drop of hydrochloric acid, however, created a current with the gold charged negatively. He concluded that "chemical action was the single cause of the current".[26]

At the same time Becquerel did not rush to conclude that every case of electricity produced by contact is due to a chemical reaction. At first, he assumed that the

[23] BECQUEREL (1823).
[24] BECQUEREL (1823a).
[25] BECQUEREL (1824).
[26] *Ibid.*, p. 178, italics added.

electromotive force and the chemical action were independent, since in some experiments the electrical effect was similar whether a metal touched water or an acid.[27] To separate the electricity originated solely in chemical reactions, he built his apparatus so as to either eliminate the electromotive forces created by contact or balance them. For instance, Becquerel took two porcelain cups filled with concentrated nitric acid and connected by an asbestos wick, and connected each of these cups to a platinum cup, filled with the same acid, using a U-shaped siphon filled with acidulated water. When platinum wires from a galvanometer were immersed in the acid in the platinum cups, there was no current. He explained the result by a balance of all electromotive forces at the various contacts: platinum/acid + acid/platinum + platinum/water + water/platinum + platinum/acid + acid/platinum.[28] Since a chemical interaction inside the siphon took place only near the entrance, the water inside it was merely a conductor. Here Becquerel assumed that without chemical action the contact of two liquids does not create an electromotive force. He concluded that "two liquids can communicate using a third one as an intermediary, without it exercising on the other two any noticeable electromotive forces".[29] He frequently used this procedure, in particular to prove that a chemical reaction between two liquids (an acid and an alkaline) also produces electricity.

Davy challenged this conclusion of Becquerel. In his view, the cause of electricity in this experiment had nothing to do with a chemical reaction between two liquids. In his own experiment, he filled one glass cup with nitre, neutral to noble metals, the other cup with concentrated nitric acid, the cups being connected with asbestos moistened with nitre. When platinum electrodes in the cups were connected to an electromagnetic multiplier, there was a strong current (a deviation of 60°), the acid side being negative. When the two liquids were nitric acid and potash, the deviation was 65°. In this instance, there was no chemical action of the fluids on each other, for they did not easily mix with the nitre, and the effect resulted from the platinum-acid and platinum-alkali contacts. When a piece of dry asbestos replaced the wet one, the acid and the alkali could meet there and react. In a short while, however, the needle stood exactly at the same point as before, which proved to Davy that no electricity was developed by the combination of the acid and the alkali.[30]

Arthur-Auguste de La Rive (1801-1873) was interested in chemical decompositions produced by a pile. Having attributed them to currents sent from the poles of a pile and spreading in the liquid, he began to investigate the intensity and direction of these currents. This brought him into collision with Volta's theory, in particular with the passive role of the liquid and the permanence of the electromotive series. He found, for instance, that changing ammonia for an acid inverted the

[27] BECQUEREL (1824a).
[28] BECQUEREL (1824b).
[29] *Ibid*., p. 31.
[30] DAVY (1826), also DAVY (1826a).

direction of the current produced by a tin-copper couple.[31] Having supposed that the acid acted more strongly on tin than on copper, while ammonia did the opposite, he generalized this rule – the metal most strongly attacked is charged positively relative to the other – and found it to be confirmed in many cases of two metals in the same liquid or in two different liquids connected by means of a third liquid. He also derived a few other empirical laws: 1) the greater the difference in the chemical action of a liquid on two metals, the stronger the current, 2) most of the resistance of a liquid comes from the resistance of metal-liquid junctions, 3) the difference in the reaction of homogeneous metals may be due to a difference in the size of the surface attacked by the liquid. Thus, from the very beginning, de La Rive assumed that the action of a metal-liquid contact was solely chemical. He asserted that electricity cannot be produced without an action (for instance, rubbing, pressing, heating) and that chemical reactions are just another such action.

From a number of experiments he concluded that: 1) contact itself does not produce an electric current if there is no chemical reaction, 2) hydro-electric current is produced by a chemical action between solids and liquids or between different liquids.[32] With one platinum electrode in nitric acid and another in potash, the two containers being connected by an asbestos wick wetted with sulfate of soda, a galvanometer showed a current, due, in Becquerel's view, to the chemical interaction of the liquids (between the acid and the salt on one side, and the alkaline and the salt on the other). Since these reactions did not produce easily visible results, to prove his point de La Rive made the wick longer: now one could see that initially the current was weak, but in a short while (when the acid met the alkali) it increased. Thus, de La Rive here upheld the idea that the stronger the reaction, the more electricity was released. He used this rule to account for the polarity acquired by two electrodes in a particular liquid. However, there were exceptions to this rule, which he tried to explain, quite vaguely, by supposing that the opposite electricities released during the reaction unite, in part, by going through the circuit in the opposite directions.

De La Rive offered a chemical explanation of Volta's condenser experiment by suggesting that the electricity observed was due to the humidity of the hand holding the plate or to the oxygen and the vapors in the air. His own experiments showed that the charge decreased when a plate was held by means of a wooden handle and also when the air was dry.

In response to de La Rive, Christian Heinrich Pfaff (1773-1852) tried to reconfirm Volta's theory by invalidating the charges raised against the condenser experiment. He repeated this experiment with a condenser made of zinc and copper plates placed under a vacuum bell. The bell was exhausted and filled with several gases, humid and dry, one by one. Since the electrometer showed the same tension, Pfaff interpreted the result as proving that the electricity observed originated at the direct contact of copper

[31] DE LA RIVE (1828).
[32] DE LA RIVE (1828a).

and zinc. Among other objections, he challenged the "chemists" to explain why the tension of a pile increased with the number of couples.[33]

Georg Simon Ohm (1789-1854) accused the opponents of the contact theory of distorting Volta's ideas, by attributing to him the claim that only the contact of different metals can be an electromotor.[34] He himself found, in agreement with Volta, that a metal-liquid contact also played an essential role. On the other hand, he denied any effect of a contact between two liquids, claimed by de La Rive and others, attributing the production of electricity in the Becquerel experiment with an acid and an alkali to the contact of the metal with these two different liquids. Like Pfaff, Ohm found the criticism of Volta's interpretation of his condenser experiment invalid. In general, he viewed the claims of the chemical theory, that all the electricity released in a voltaic circuit is due to chemical changes, as exaggerated.

Unlike Pfaff, Stefano Giovanni Marianini (1790-1866), physics professor in Venice, undertook a comprehensive review of de La Rive's paper, looking for weak spots in the chemical theory and answering objections against the contact theory.[35] In particular, Marianini suggested a new explanation of the change in polarity some couples showed in different liquids, for instance copper was negative relative to tin in an acid, but became positive in ammonia. According to de La Rive, the reason was that the acid attacks copper less vigorously than tin, while ammonia reacts more strongly with copper than with tin. In Marianini's view, the change of polarity observed when the couple was moved from an acid to ammonia came from a change in the metals' electromotive forces: ammonia increases the electromotive force of tin and decreases that of copper. In a similar way, two identical zinc plates affected a galvanometer if one of them was immersed in an acid earlier than the other. The first plate had undergone a change by the time the second plate was submerged, thus they became heterogeneous, and, according to Volta's theory, could create an electromotive force.

To Marianini, heterogeneity was the only source of electricity. He considered various sources of heterogeneity, such as a difference in the size of a surface covered by a liquid, or a difference in temperature of the two bodies. He criticized the chemical theory for not explaining why tension depends on the number of couples, or why it does not change with a change in the liquid. In his view, the chemical theory was no better that the contact theory:

> Even if Volta's theory were a pure hypothesis, that is if it did not rest on incontestable facts, or if the accord observed between these facts and the phenomena of the pile were simply fortuitous, since it offers an easy explanation of all the phenomena, it would be preferable to the electrochemical theory which does not at all offer a *plausible* explanation of many of these phenomena.[36]

[33] PFAFF (1829).
[34] OHM (1831).
[35] MARIANINI (1830).
[36] *Ibid*., p. 154, italics added.

However, Marianini made the point that his theory differed from that of Volta:

> In the voltaic theory recalled here one considers an electric current excited by an electromotor to be the result of simple currents which tend to create various circumstances, or of electromotive forces in conflict in the electromotor itself, such as the contact of metals among themselves and with liquids, the contact of two liquids, etc.[37]

Like Marianini, Karl Johann Karsten (1782-1853) gave prominence to liquids.[38] According to him, metals and other solid bodies immersed in a liquid are electrified positively with respect to the liquid, and of the two metals, the weaker electromotor acquires a negative charge. Strangely, though, he claimed that the part of the metal above the liquid obtained a charge opposite to that of the submerged part. To Karsten, the true moving force was the difference between the electromotive forces created in two liquid-metal contacts. He supposed the electromotive actions to be based on continuous separation and neutralization of the opposite electricities, which was in agreement with chemical changes in the circuit, but not being an effect of these reactions.

When Faraday first entered the debate in 1834, he was not yet well familiar with the current situation and believed that any experiment in which electricity was created without the mutual contact of two metals would be sufficient to overthrow the contact theory. Accordingly, he devised the following ingenious experiment in which a platinum plate and a zinc one are placed horizontally at a very small distance from one another.[39] They were electrically connected at the ends by a drop of an acid and by a drop of potassium iodide. As soon as this circuit was closed, a coloration appeared showing that there was a current which decomposed the potassium iodide. Among other arguments in favor of the chemical theory, Faraday relied on his law of electrolysis.

Faraday's "crucial" experiment, however, did not impress the "contactists" at all, because, as Johann Christian Poggendorff (1796-1877) noted, a metal in contact with two different liquids became heterogeneous and thus, according to Volta, was an electromotor.[40] Poggendorff considered the total electromotive force in this experiment to be equal to the difference between the electromotive forces of each metal with the two liquids. He showed that the total electromotive force depended in its magnitude and polarity on the choice of the two liquids, and in many cases did not correlate with the chemical affinity. As to the law of electrolysis, Poggendorff remarked that it held true for a current of any origin – he himself verified it for an induction current – and thus could not prove the chemical origin of electricity in a voltaic circuit.[41]

In 1836, de La Rive modified his theory to answer several objections and also provided additional experimental support for it. In particular, he addressed the issue

[37] *Ibid.*, p. 155.
[38] KARSTEN (1835).
[39] FARADAY (1834), § 626 (§ 891 in the original edition).
[40] POGGENDORFF (1840), p. 488.
[41] POGGENDORFF (1838).

of the tension of the pile. His solution did not show, however, that the tension between the ends of a pile was greater than that of a single couple. While his discussion of the pile was not satisfactory as a whole, one point deserves our attention. When trying to explain why a continuous chemical reaction did not lead to tension of unlimited magnitude, de La Rive supposed that part of the opposite electricities separated by the reaction and released at the electrodes recombined through the liquid.[42] Actually, this resembles the modern idea, although expressed in different words, that the more ions are released at an electrode, the stronger they repel those that follow them, until equilibrium is established.

De La Rive formulated three principles of the chemical theory: 1) electricity is produced when two heterogeneous bodies in contact with one another are placed in a liquid or gas which reacts chemically with at least one of them, 2) electricity is not produced when there is no chemical action, nor a mechanical nor a thermal effect, 3) the "intensity" of the electricity produced is not always proportional to the rate of the chemical reaction which creates it, and can be modified in part by immediate recomposition of the two electricities and by the nature of the chemical reactions. The latter principle aimed at explaining why sometimes a strong reaction created a lesser current than a weak one, why the current changed its magnitude and even its direction with time, and why a current was created even when the metals apparently did not react with the liquid.

One of the difficulties in the debate was the ambiguity of certain terms. In particular, it was not clear how to define the "strength" of a chemical reaction: by its rate, the amount of substances produced, etc. For this reason, de La Rive's law that, of the two metals immersed in a liquid, the one which is attacked more strongly is charged positively, became an easy target for criticism, for it was known that sometimes the metal releasing less gas became positive.

Likewise, the very presence of a chemical reaction was not always obvious. For instance, when Marianini claimed to have observed a current created by gold and platinum plates in nitric acid, which was known to be neutral to these metals, de La Rive blamed impurities in the metals used by Marianini, because his own experiment did not show any current. Marianini, in turn, suggested that de La Rive's galvanometer was not very sensitive. Another examples is Becquerel's observation of the production of electricity by a couple of inactive substances, such as platinum and manganese peroxide. De La Rive demonstrated that manganese peroxide forms a hydrate when in contact with water, which led him to the idea that "one must not deny the presence of a chemical action because one does not immediately see the products".[43] Consequently, he supposed that some chemical changes, such as tarnishing (oxidizing) of metals, may be not readily noticeable. And if the eye, he said, is not the best judge of slow chemical reactions, perhaps we had better reverse

[42] DE LA RIVE (1836), p. 189.
[43] DE LA RIVE (1836a), p. 159.

the procedure: let us assume a proportionality between the degree of affinity in a particular reaction and the current produced and use a galvanometer to search for "invisible" chemical processes.

Responding to Faraday and de La Rive, Marianini asserted that the production of electricity by identical metals plunged in the same liquid did not invalidate his theory, for it was enough to suppose that the liquid made the metals heterogeneous (for instance, by immersing them not simultaneously). If the metals remained homogeneous, there should be no electricity in either theory.[44] Marianini viewed the attempt of de La Rive to remove the proportionality between the intensity of electricity and that of a chemical action as a sign of a weakness in the chemical theory. He had no difficulty in explaining his gold-platinum experiment: the current was weak because the metals were close to one another in their electromotive ability, and when eventually the current disappeared it was because the acid changed the electromotive forces of the metals so as to make them less different. However, to explain why the current did not disappear when both plates were connected some time after their immersion, he supposed that the changes in the electromotive forces went in the opposite directions. Marianini did not accept the "invisible" reactions. To him, all cases of electricity produced without a noticeable chemical effect spoke of an insufficiency in the chemical theory. He also objected to de La Rive's idea of a partial recombination of electricity, for he did not see that increasing the resistance of a pile augmented its tension.

A new twist to the connection between the production of electricity and chemical activity was added by Christian Friedrich Schönbein (1799-1868), professor of chemistry at the University of Basel. He rediscovered the phenomenon of "passive iron", in which an iron wire immersed in concentrated nitric acid loses its ability to precipitate copper from a solution of copper sulfate.[45] The passive iron coupled with platinum did not produce any current. Its chemical activity could be restored, however, if the passive wire and a common iron wire were partially immersed in dilute nitric acid and then connected above the level of the liquid. If the restored iron and platinum were placed into a solution of copper sulfate, a current developed and both metals were covered with copper. Schönbein considered this phenomenon to be a strong argument in favor of the chemical theory.

He also offered another explanation for the electricity produced without any apparent chemical activity. The solution, he said, was in redefining "chemical activity":

> One says that two contacting substances do not act chemically if they do not produce any qualitative changes [...] In chemistry, one can pose as an axiom the principle that every time that heterogeneous substances come into contact, the forces of attraction [...] come into activity between them, whether these forces produce a chemical separation or not. We must also admit in the cases when one does obtain a chemical result that, before one obtains it,

[44] MARIANINI (1841), p. 529.
[45] SCHÖNBEIN (1836).

> chemical attraction has already begun to act [...] If now this *tendency* to decomposition is actually not realized, it must not be considered because of this as non-existent.[46]

Schönbein realized that this hypothesis put him at odds with other "chemists":

> They [Faraday and de La Rive] consider only such chemical activity as capable of setting the electricity in motion, [...] which is accompanied by a material result [...] I claim, on the contrary, that the mere tendency of two bodies to combine is already capable of destroying their electric equilibrium even if their real combination does not take place.[47]

That Schönbein's "tendency" was a sound idea one can see from its resemblance to the contact potential hypothesis developed 50 years later by Oliver Lodge, yet it was not accepted in the 1840s or even later.

Gustav Theodor Fechner (1801-1887), professor at the University of Leipzig, was not satisfied with the new arguments by the "chemists". He upheld Marianini's view that liquids modify the electromotive force of metals immersed in them. In particular, he applied this idea to explain Schönbein's experiment with passive iron and platinum. While speaking of invalidating Volta's condenser experiment, he emphasized that references to friction or pressure could not invalidate Volta's theory, because these contact phenomena, as well as thermoelectricity, remained unexplained in the chemical theory either.[48]

From his study of the role of liquids, Fechner concluded that: 1) liquids exhibit considerable electromotive forces when in contact with metals and with one another, 2) the opposite electricities originated at the surfaces in contact produce secondary effects (including chemical) between metals and liquids, which modify the charge on the condenser so that the overall result of these secondary effects is as if the liquids were merely conductors without any electromotive action, so that everything might depend on the action of metals on one another.[49]

Faraday's second entrance into the debate in 1839 was much better prepared than the first one.[50] Having realized the flexibility of the contact theory, he no longer relied on an *experimentum crucis*, trying instead to build a vast and logically organized system of experiments in support of de La Rive's theory. First, he targeted a number of flaws in the contact theory. In particular, he challenged as unproven Volta's law that the total electromotive force of a chain of conductors equals that created by its extreme members. On the other hand, he tried to plug some holes in the chemical theory, such as explaining why the tension of an open pile increases with the number of couples. In this, Faraday was no more successful than de La Rive. Being uncertain about the power of physical arguments, Faraday added a metaphysical one, namely that the contact theory advocated "a production of power

[46] SCHÖNBEIN (1838), pp. 156-7, italics added.
[47] *Ibid*., p. 161.
[48] FECHNER (1838).
[49] FECHNER (1839), pp. 262-3.
[50] FARADAY (1839).

without a corresponding exhaustion of something to supply it".[51] That was one of the early qualitative formulations of the conservation of energy.

Faraday's intervention, however, did not convert the "contactists". In Poggendorff's opinion, de La Rive and Faraday had failed to prove the main principle of the chemical theory: "if there is no chemical activity, there is no current".[52] He offered new examples of electrical currents obtained without any noticeable chemical reactions, such as from the iron-platinum couple in potash solution. The current considerably increased when platinum was placed in nitric acid and iron in potash solution, the liquids being separated by a porous clay wall. While usually this case was cited as supporting the chemical theory, because the liquids strongly interacted with one another, in Poggendorff's view, the fact that the current was independent of the size of the surface where the liquids contacted one another suggested that the reaction was only one of its causes, the mutual electromotive action of the liquids being the other one.

Another objection came from Eugene Péclet (1793-1857), who extensively experimented with measuring tension in voltaic circuits by means of a condenser electrometer, something which Faraday had totally neglected. Péclet, concluded that, since neither friction nor pressure nor chemical changes could explain his results, this electricity had to be a contact phenomenon.[53] While acknowledging that in many cases chemical activity did stand behind the electricity produced, he insisted that in the cases in which there was no known chemical action one had to attribute the electricity developed to the influence of a contact. Possibly in response to Faraday, he tested Volta's law for a chain and found it correct, and not only for metals but also for liquids. In Péclet's view, Volta's theory should have been corrected, since the effect of a metal-metal contact was less important than that of a liquid-metal.

By the mid-1840s, the controversy was essentially over, apparently without resolving the problem. Or, does an inconclusive outcome of a debate necessarily mean the absence of a solution? We will see that the debate did have an outcome, perhaps an unexpected one: the two theories moved towards one another.

5. Merging Two Theories

Winning an argument may not be equivalent to resolving a problem. Likewise, not winning an argument does not necessarily mean the absence of a solution. A belief that the debate on the origin of voltaic electricity was somehow resolved or not in the 1840s depends on the meaning of the phrase "resolving a scientific dispute". If it means the pronouncements made by the participants in the debate at the time, the

[51] *Ibid*., p. 314, § 1059 (§ 2071 in the original edition). See also FARADAY (1843), p. 479.
[52] POGGENDORFF (1841).
[53] PÉCLET (1841).

conflict was not resolved, for neither theory was accepted as the winner by both camps. However, if we speak of an *impact produced on science*, even if not recognized by the participants right away, then we find sufficient evidence that the problem was solved, and it was done by a rapprochement of the two theories.

One aspect of this rapprochement can be seen in gradual changes in the theoretical views of representatives of both camps. For instance, while Davy switched from the chemical theory to the contact one, Becquerel slowly moved in the opposite direction. In 1834, he was still attempting to find some role for the contact theory:

> in the contact of bodies, in almost all cases, there is a chemical action, and one is inclined to believe that the latter cause exercises the most influence on its production. Nonetheless, in the current condition of science one must not yet abandon Volta's theory.[54]

In 1842, however, he concluded that "the electricity released by the pile *totally* originates from chemical action".[55] He attempted to generalize the condition for releasing electricity at a contact: "thousands of experiments have proven that there are no electrical effects of contact unless there is a chemical or calorific action, or any derangement of the natural position of molecular equilibrium".[56] It is not clear, however, how to recognize the existence of this derangement other than through the electric effect. He believed that "when two bodies having an affinity to one another are in contact without their combining, it can happen that the effect of chemical forces beginning to act distorts the equilibrium of molecules and releases a small quantity of electricity which is not capable of producing continuous electric currents".[57] He came to this idea under the influence of the following experiment by his son, Alexandre Edmond Becquerel (1820-1891):

> When one substance acts on another under the influence of light, electrical effects are produced as in all chemical reactions, which effects are manifested as long as this influence persists. If it stops, there is no sign of electricity, although the contact of the substances newly formed with the metal plates still exists, and nothing has changed in the circuit. This experiment, which we regard as fundamental [...] shows thus that a contact that is not followed by a chemical action would not distort the electrical equilibrium. Light can aid in solving this question because it allows the chemical action to appear or disappear without destroying the contact, a condition which cannot be satisfied by ordinary chemical agents.[58]

One could have objected that light can release electricity directly as heat does in a thermoelectric circuit, without a chemical intermediary. What is important, however, for our purpose is not how convincing Becquerel's example was for others (incidentally, no one raised this objection at the time), but his tendency to find in the contact a relation between three concepts: physical contact of two bodies, distortion

[54] BECQUEREL (1834-40), II, p. 145, italics added.
[55] BECQUEREL (1842), I, p. 69, italics added.
[56] *Ibid.*, p. 68.
[57] *Ibid.*, pp. 68-9.
[58] *Ibid.*, p. 70.

of the electric equilibrium of their molecules, and a chemical reaction.

Carlo Matteucci (1811-1868) also began as a "contactist", who used a prepared frog to prove that a metal contact alone, without any chemical action, can create electricity.[59] Five years later, however, when research led him to the law similar to Faraday's law of electrolysis, he was willing to admit that chemical action and the electromotive force are the same.[60] And eventually he gave all the credit for producing electricity to chemical action alone.[61]

While other "contactists" did not convert to the chemical theory, they changed their own theory. The most important modification was acknowledging the active role of the liquid: Marianini, Pfaff, Karsten, Fechner, Poggendorff, Péclet and others held that a metal-liquid contact or sometimes even a liquid-liquid contact can generate electromotive power comparable to or even exceeding that of the contact between two different metals. They differed among themselves, however, about the relative force of these different electromotors and frequently disagreed about the explanation of the same phenomenon. Several of them also maintained that, as shown by a galvanometer, with time, a liquid can change the electromotive force of a voltaic couple immersed in it. Incidentally, no one noticed that this explanation was incompatible with the results obtained by means of an electrometer. Thanks to these two modifications, Volta's theory once again became very flexible. The chemical theory, though, was not far behind in adapting to the new challenges. In particular, the "chemists" invented several ways to counter the main objection that there should be no current if there is no chemical reaction.

Another aspect of the rapprochement is seen in focusing on the easily adaptable concepts within each theory. Let us consider the idea of *changing* the electromotive force of a metal by immersing it in certain liquids. The "contactists" did not say why such a change takes place, but what other possible *cause* for this change could there be but a chemical reaction? Thus, in one theory we have: "two copper wires immersed in an acid one after the other produce electricity, because they interact chemically with the acid differently", while in the other theory the same effect is explained as: "two wires produce electricity by contact because they are heterogeneous, and they become heterogeneous when immersed in the acid at different times". We see that the two explanations are fully equivalent, the difference is semantic with the "change" in one corresponding to the "chemical change" in the other.

The same happens when the main seat of the electromotive force is moved to a metal-liquid contact. Where a "contactist" would say that "some force at the contact of a metal and a liquid creates electricity", a "chemist" would say the same but replacing "some force" with "chemical affinity". Again, for those willing to accept it, the difference between the two expressions may be viewed as only semantic. And,

[59] MATTEUCCI (1830).
[60] MATTEUCCI (1835).
[61] MATTEUCCI (1852).

in fact, there was good reason for expecting such willingness to come. In the 1820s, the contact theory had an important advantage over the chemical theory: simplicity. The "chemists" promised more than they could deliver, for their knowledge of chemical reactions was insufficient to arrive at any true general laws connecting these reactions with a release of electricity. The "contactists" were content with asserting the existence of the contact force, without inquiring into its nature, and with finding empirical laws, such as the electromotive series. By the 1840s, the understanding of chemical reactions had improved and with it the possibility of predicting the character of the current produced; so the agnostic position of the "contactists" was no longer justified by lack of knowledge. Thus a movement began (Becquerel, Matteucci, and others) to assume that the contact (electromotive) force and the chemical force are the same.

There was also another, perhaps even more important, reason for this willingness to compromise. By the 1840s, it became clear that solving the original problem exceeded the capability of contemporary science (as Ostwald noted, it took fifty years more to understand some basics of the electrochemical process). A common sense option open was to forget about the nature of the phenomenon and concentrate on the phenomenon itself and the laws directly deducible from experiments. Within such an empirical framework the contact theory had something positive to offer.

By the early 1840s, each side had already proven the "insufficiency" of the rival theory, but only to itself, for opponents countered the new objections quite easily. As a result, the controversy died out, with researchers turning to other objects and leaving scientists to form their own opinions on the matter.[62] On the other hand, negative arguments did not exhaust the opportunities of the two theories, since each also had something constructive in it. The chemical theory, for instance, could predict the relative magnitude and direction of the current in some experiments, while the "contactists" were capable of a meaningful interpretation of their measurements, at least in some cases. Thus, although neither theory could explain all the phenomena, there was something uniquely valuable in each. And this created conditions for an eventual merger.

One of the outcomes of the debate was that a group of the "contactists" (Ohm, Poggendorff, Kohlrausch and others) redefined their purpose in voltaic research. Instead of qualitative experiments, primarily of a chemical nature, the results of which they could not present unambiguously and convincingly, they moved on to quantitative experiments, mostly physical by nature, based on the concept of electromotive force and Ohm's law, where the results were much more certain. Among these applications we see electrochemical polarization, the compensation method to measure the electromotive force, verification of Ohm's law, etc.[63] The ability of the contact theory to be quantified was its main advantage over the

[62] OSTWALD (1980), II, p. 735.
[63] POGGENDORFF (1843); POGGENDORFF (1847); JACOBI (1842); KOHLRAUSCH (1852).

chemical theory. Volta started this approach by supposing that the electromotive force of an open pile was proportional to the number of couples, and Ohm extended it to a closed circuit, by connecting current, tension and resistance.

Another result of the controversy was a move on the part of some "chemists" to incorporate some ideas of the contact theory into the chemical theory. The quantitative aspect of the contact theory had always been the subject of envy on the part of some of its opponents. For instance, in 1842 Becquerel noted that:

> the only advantage of this theory is to provide a simple principle for mathematical analysis, with the aid of which one can deduce in some specific cases the results of experiment from the equations containing arbitrary constants. It is one of the reasons which have contributed to keeping this theory in science.[64]

After passive recognition came direct borrowing, and Schönbein was the first to do it. He suggested that the time had come to stop the dispute, which had become too personal, in the name of "love of truth rather than self-love".[65] This was not, however, a call for a truce to sustain the status quo without useless public discussion. On the contrary, he was convinced that the preponderance of evidence was in favor of the chemical theory. In particular: 1) the contactists were guilty of not recognizing the intimate connection between chemical and electrical phenomena, which is so transparent in many experiments, 2) the contact theory did not allow one to predict the result of experiments regarding the magnitude of current and its direction, 3) it introduced a new force, the strength of which has no definite relation to the mass of matter, and which implied "uninterrupted work", with the latter probably referring to a *perpetuum mobile.* But his most important reason for disposing of the contact theory was the possibility to explain by the chemical theory – finally! – why the electromotive force (he used the term *Spannung*) of an open pile increases with the number of couples.

The essence of his explanation is similar to the modern one. Let us consider a cell filled with water, with zinc and platinum electrodes. Due to chemical attraction, a zinc plate polarizes a molecule of water adjacent to it, which in turn polarizes the next molecule, and so on, with all molecules in a row having the same magnitude and polarity of *Spannung*. If the platinum electrode is connected to water in another cell, the polarization of water molecules will continue. However, if the second cell contains another zinc-platinum couple, then it will provide an additional *Spannung* of the same magnitude and direction, which will increase the degree of polarization of each molecule of water two times, and so on. Some features of this theory invite calling it a "rapprochement". One is that for the first time a "chemist" employed the concept of *Spannung*, or electromotive force, borrowed from the "contactists". The other is the freedom to assign the seat for it. For more than two decades, the opponents had argued whether electricity was released at the metal-metal junction or at the metal-liquid one, until Schönbein suggested that:

[64] BECQUEREL (1842), I, p. 68.
[65] SCHÖNBEIN (1849), p. 305.

> it is *completely indifferent* whether one moves the seat of electromotive force here or there in the pile and deduces this force from chemical affinity or something else, because one or the other hypothesis requires that the Spannung of the pile would rise with an increase in the number of its elements.[66]

The implication is that, as long as we are concerned with the quantitative aspect of the voltaic phenomena, we can forget our differences about its nature. The importance of this idea cannot be overestimated, because it was the first step in transforming the chemical theory of voltaic phenomena into a quantitative theory, without which it would not have survived into the second half of the nineteenth century. Apparently, the same need to quantify voltaic circuits guided de La Rive in his book on electricity published in 1856.[67] He defined the electromotive force in two ways, theoretical and practical, that is, independent of theoretical interpretations. In the former, it was defined as "the force with which the molecules of a liquid [...] are polarized due to chemical affinity".[68] In the latter, it was "the force which produces electricity in a voltaic circuit, leaving aside the resistance of this circuit"[69] (resistance is mentioned because the electromotive force is measured by a galvanometer). Within this framework, the "chemist" de La Rive had no problem using Ohm's law.

The third and final outcome of the debate was its impact on teaching physics: the textbooks were the first to offer a constructive way to merge the two theories into a "compound" one.

As early as 1840, Gabriel Lamé (1795-1870), Professor at the École Polytechnique, stated that "Volta's ideas about the cause of the development of electricity in the pile can no longer be supported, and [...] chemical actions have a great part in its development, if they do not form its single and unique cause".[70] Since he was not certain about a chemical explanation of a few cases, Lamé suggested that:

> one can adopt the chemical theory of the pile without denying for this purpose that it is possible to produce free electricity by a single contact of certain bodies; one must only consider the latter cause as playing a very small part in voltaic phenomena.[71]

Johann Müller's 1845 textbook provided an overview of both theories, noting about the contact theory that it "must be corrected and extended to explain the newly discovered facts, otherwise, one will have to abandon it completely and establish a totally new hypothesis".[72] In another place he added that since it was very difficult to account for all phenomena in the "extreme" version of either theory, "in the current situation of science, the best means can be a *modified contact* theory, [...] because in

[66] *Ibid*., p. 296, italics added.
[67] DE LA RIVE (1856-8).
[68] *Ibid*., II, p. 721.
[69] *Ibid*.
[70] LAMÉ (1840), III, p. 110.
[71] *Ibid*., p. 111.
[72] MÜLLER (1845), II, p. 163.

this way various phenomena of the circuit can be best summarized from a common viewpoint".[73] The meaning of this "common viewpoint" comes from a lengthy passage from an article by Buff cited by Müller:

> According to the electro-chemical theory, the current is a condition of a disrupted chemical equilibrium, while in the contact theory it is a condition of a disrupted electrical equilibrium. And here in fact lies the whole essential difference between the two theories, a difference reduced only to the form of expression. Still, this difference is not insignificant, for it gave the contact theory a preference in accounting with ease for both static and current phenomena in hydro-electric circuits.[74]

It is not clear how he realized this program in teaching the subject, except for providing Ohm's law, the reference to which in the last sentence is quite transparent. We see the details in subsequent editions of his textbooks. Although Müller noted that the identity of the electrical and chemical attraction had not yet been "fully proven", the electrochemical theory was the only one he presented. Nonetheless, when coming to the quantitative part, he preferred to treat the theory as an empirical one.[75] In this "empirical" theory, he placed the seat of the electromotive force at the metal-liquid contact, and the difference of potentials between the electrodes (the author uses "charges") came as the difference of their potentials relative to the liquid. The explanation of the electromotive force of the pile was also very similar to that in a modern textbook.[76] In other words, the author operated with the electromotive force as a given quantity, without asking about its origin.

This approach to the pile became standard in textbooks at both high school and university levels: chemical reactions were pronounced to be the only source of voltaic electricity, and the quantification of the theory was based on the electromotive force and Ohm's law.[77] While the authors believed they were presenting the chemical theory, in terms of the 1830s, it was a compound of the chemical and the contact theories. The history of the debate seldom appeared in textbooks, and if it did, the contact theory was easily dismissed, sometimes as contradicting energy conservation.[78] Whether the authors who did not mention the contact theory at all were guided by the same reason, is not clear. It is unlikely that this reason became significant prior to the 1860s. For instance, de La Rive did not bring up the conservation law in his 1856 book on electricity, although he continued to debate there the contact theory. It is very likely that the energy conservation argument was added later, and the original decision to eliminate the contact theory (at least in its older form) from teaching was made on the grounds discussed above.

[73] *Ibid*., p. 164, italics added.
[74] *Ibid*., p. 166.
[75] MÜLLER (1869), p. 399.
[76] *Ibid*., pp. 382-3.
[77] PRIVAT-DESCHANEL (1873), pp. 643, 675-7; OLMSTED (1870), p. 276.
[78] VERDET (1868-69), p. 393.

6. Conclusions

The debate on the nature of voltaic electricity provides better insight into the significance of Volta's theory. While Volta's vague "contact force" was eventually rejected as a cause of voltaic electricity, his other ideas, such as quantification of the pile's effects and the concept of the electromotive force fully proved their value in physics during the first half of the nineteenth century.

The debate also supplies evidence that improves our understanding of the relationships between theory and experiment. First, it shows that opinions about an experiment supporting or contradicting a certain theory are subjective. When during the debate one side offered experiments presumably contradicting the rival theory, the other side reinterpreted these experiments as supporting the theory. Second, while at the time scientists did believe in the decisive role of an *experimentum crucis* in choosing between competing theories, in the absence of such they were willing to settle on other criteria as well, such as the *amount* of evidence offered by both sides. Third, when the discussion was qualitative, each theory could be modified to cover new experiments. Fourth, if the problem did not appear solvable, scientists simplified it to bring it within reach of existing concepts and tools and try to resolve at least part of it. Finally, one way of resolving a conflict between two theories may be in finding a middle ground by combining the most valuable elements of both theories.

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