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## **Confusion and Controversy: Nineteenth-Century Theories of the Voltaic Pile**

### **1. Introduction**

In his important study of Robert Mayer – and the emergence of the law of energy conservation, Kenneth Caneva dealt briefly with the controversy that raged for more than half a century concerning the explanation of Volta's electrical pile. His remark, that "This subject is in need of a major historical study" is no less justified in 1999 than it was in 1993, when Caneva wrote his book.<sup>1</sup> In spite of a few historical works that touch the subject the situation is still that Wilhelm Ostwald's impressive but nonetheless outdated volumes of 1896 are the best, and by far the most detailed, account of the controversy.<sup>2</sup>

What makes the voltaic controversy both interesting and unusual is its long duration and complex structure. It was essentially over the explanation of Volta's pile but can be traced back to before 1800 when it was part of the better known Galvani-Volta controversy (section 2). From the 1790s to the 1840s the question divided scientists into two camps, one of which defended Volta's notion of a contact force and the other of which argued that the cell could be better explained in

<sup>1</sup> K.M. CANEVA, *Robert Mayer and the Conservation of Energy*, (Princeton, 1993), p. 372. Among the few works, apart from Ostwald's, that deal with the history of the controversy are C.J. BROCKMAN, "The Origin of Voltaic Electricity: The Contact vs. Chemical Theory before the Concept of E.M.F. was developed", *Journal of Chemical Education*, 5 (1928), pp. 549-55; and J.R. PARTINGTON, *A History of Chemistry*, 4 vols., (London, 1961-70), IV, pp. 123-41. Other relevant works will be mentioned below.

<sup>2</sup> W. OSTWALD, *Electrochemistry: History and Theory*, 2 vols., (New Delhi, 1980), a translation of *Electrochemie: Ihre Geschichte und Lehre*, (Leipzig, 1896). Ostwald's massive work is a unique source for the study of the history of electrochemistry, but one which should be read with critical eyes. It reflects very much the positivistic climate of the age and also that the author was himself part of the history he wrote. It should be noted that the extensive quotations (almost half the book) are mostly based on German translations and not the original sources, for which reason they are not always accurate. For an analysis of Ostwald's work, see G.S. MORRISON, "Wilhelm Ostwald's 1896 History of Electrochemistry: Failure or Neglected Paragon?", in G. DUPBERNELL and J.H. WESTBROOK, eds., *Selected Topics in the History of Electrochemistry*, (Princeton, 1978), pp. 213-25.

chemical terms (section 3). The recognition of the principle of energy conservation around 1850 did not settle the matter, although it did change the focus and intensity of the controversy (section 4). In a modified form it was revived in the 1880s, now with new actors and focusing on the question of the existence of contact potential (section 5). It is a most remarkable feature that none of the great theoretical breakthroughs of the century – such as energy conservation, the second law of thermodynamics, the ionic theory of dissociation, and the discovery of the electron – had a decisive influence on the controversy. It lived on, apparently endlessly, into the twentieth century when it was finally resolved, at least in a way. But the resolution was undramatic, little noticed, and, in a historical perspective, somewhat of an anticlimax. It was a resolution that would not have satisfied the scientists who were engaged in the controversy during its most heated period in the 1830s. In what follows I shall concentrate on the nineteenth century and, in the conclusion, consider the controversy in a larger perspective, pointing out some of the philosophical and historiographical aspects that may be illustrated by the case (section 6).

## 2. The Roots of the Controversy

The notion of electrical action generated by metallic contact was first proposed in a work dated 1789 by the British natural philosopher Abraham Bennet.<sup>3</sup> However, it was only with Volta's independent theory that the idea became of importance in the development of electrical science and, several years later, the generally accepted explanation of the pile. Volta's first version of the contact theory appeared as early as 1792, in the form that metals "[are] true motors of electricity, for with their mere contact they disrupt the equilibrium of the electrical fluid, remove it from its quiescent, inactive state, shift it, and carry it around".<sup>4</sup> During the following years he changed his ideas on the subject somewhat, but not essentially. The important point is that the contact theory remained the core element in Volta's dispute with Galvani and his attempt to replace animal electricity with metallic electricity.

By 1796 Volta had reached the definitive formulation of his theory, namely, as he wrote in his second letter to Friedrich Gren, the German chemist and publisher of the *Neues Journal der Physik*: "The contact between, for example, silver and tin gives rise to a force, an exertion, that causes the first to *give* electrical fluid, the second to *receive* it: the silver tends to release it, and releases some into the tin, etc. If the circuit also contains moist conductors, this force or tendency produces a current, a continuous flow of the fluid, which travels in the above-mentioned

<sup>3</sup> According to E. WHITTAKER, *A History of the Theories of Aether and Electricity*, 2 vols., (London, 1951), I, p. 72, Bennet was known as the inventor of the gold leaf electroscope (1786) which played an important role in the Galvani-Volta controversy.

<sup>4</sup> Quoted from M. PERA, *The Ambiguous Frog: The Galvani-Volta Controversy on Animal Electricity*, (Princeton, 1992), p. 110.

direction from the silver to the tin, and from the tin via the moist conductor(s) back to the silver and then back to the tin, etc. If the circuit is not complete, if the metals are insulated, the result is an accumulation of electrical fluid in the tin at the expense of the silver ...".<sup>5</sup> He had, he told Gren, originally been inclined to believe that "the action setting the electric fluid in motion is derived not from the mutual contact of two metals but from the contact of each of these metals with the damp conductors".<sup>6</sup> New experiments had forced him to abandon this idea. Volta realized that the moist conductor – the electrolyte, to use a later expression – was required for the production and transmission of the current, but he now emphasized that the seat of the electricity was the metal-metal junction and not the contact between metal and liquid. The force that caused the charge separation was postulated rather than explained, but at least Volta could coin a name for it, the *forza motrice* or electromotive force, a term that was introduced in 1796. In 1801 he defined the new force as a measure of the disturbance of the equilibrium of electricity between two metals, equal to the tension in an open circuit.<sup>7</sup>

When Volta constructed his pile in late 1799 he inevitably conceptualised it in terms of the contact theory which from the very beginning became the theoretical basis on which he explained the new apparatus. The close connection between the pile and the theoretical concept of contact electrification was reflected in the title of Volta's famous letter of 20 March 1800 to Joseph Banks – "On the Electricity Excited by the Mere Contact of Conducting Substances of Different Kinds".<sup>8</sup> Volta wrote that the superior conductivity of salt water was "one of the reasons, if not the only one, why it is so advantageous that the water of the basin, and, above all, that interposed between each pair of metallic plates, as well as the water with which the circular pieces of pasteboard are impregnated, &c. should be salt water ...".<sup>9</sup> In all his later publications he maintained that the action of the pile was due solely to contact between the metals and that the humid conductor merely served to ease the passage of the current. Diluted sulphuric acid or salt water, he wrote in 1802, were

<sup>5</sup> PERA, cit. 4, pp. 143-4 (*VO*, I, p. 419). For Volta's earliest conception of the contact theory and its role in the Galvanic controversy, see also S. GILL, "A Voltaic Enigma and a Possible Solution to It", *Annals of Science*, 33 (1976), pp. 351-70; and J.L. HEILBRON, "Volta's Path to the Battery", in DUPBERNELL and WESTBROOK, cit. 2, pp. 39-65.

<sup>6</sup> OSTWALD, cit. 2, I, p. 57.

<sup>7</sup> R.N. VARNEY and L.H. FISHER, "Electromotive Force: Volta's forgotten Concept", *American Journal of Physics*, 48 (1980), pp. 405-8.

<sup>8</sup> The letter was in French (*VO*, I, 565-82). An English translation appeared in *Philosophical Magazine*, 90 (1800), pp. 403-31 and can more conveniently be found also in B. DIBNER, *Alessandro Volta and the Electric Battery*, (New York, 1964), pp. 111-31. See also G. SARTON, "The Discovery of the Electric Cell (1800)", *Isis*, 15 (1931), pp. 124-57, which includes on pp. 129-57 a facsimile of Volta's letter in the *Philosophical Transactions of the Royal Society*.

<sup>9</sup> DIBNER, cit. 8, p. 115.

known to be excellent conductors and they “are applied ... for no other purpose than to effect a mutual communication between all the metallic pairs”.<sup>10</sup>

Although Volta knew that the action of the pile was associated with chemical phenomena, he preferred not to mention these, probably because he feared that they might undermine his purely non-chemical contact explanation. In 1792 a chemical alternative to both Galvani’s and Volta’s theories had been presented by Giovanni Fabbroni, who suggested that galvanic phenomena were connected with and possibly caused by the oxidation of the metals.<sup>11</sup> Fabbroni’s idea, translated into French and English in 1799, was taken up by William Nicholson and Anthony Carlisle who built the first voltaic pile outside Italy and in an important experiment of June 1800 observed that the electricity generated by the pile decomposed water into hydrogen and oxygen.<sup>12</sup> Another scientist who developed Fabbroni’s suggestion was Humphry Davy, who later in 1800 concluded that “the oxydation of the zinc in the pile, and the chemical changes connected with it are *somehow* the cause of the electrical effects it produces”.<sup>13</sup> This was a direct challenge to Volta’s contact theory. Although Davy soon changed his mind, there were others who opposed Volta’s explanation and argued that the pile was in reality a chemical machine. According to these, not only did the pile produce chemical effects, which was an uncontroversial fact, but its action was also caused by chemical processes.

Among the earliest and most important of the electrochemists was the German Johann Ritter, a *Naturphilosoph* who has sometimes been called the father of electrochemistry.<sup>14</sup> Ritter believed that “the phenomena of galvanism might very well belong to the same class as those of chemistry”, as he wrote in 1798, before Volta’s invention of the pile.<sup>15</sup> In 1800 he had provided sound experimental

<sup>10</sup> PERA, cit. 4, p. 159.

<sup>11</sup> G. FABBRONI, “On the Chemical Action of Different Metals on Each Other at the Common Temperature of the Atmosphere”, [Nicholson’s] *Journal of Natural Philosophy, Chemistry and the Arts*, 3 (1799), pp. 300-10; 4 (1800), pp. 120-7. An English translation also appears in OSTWALD, cit. 2, I, pp. 102-10.

<sup>12</sup> W.M. SUDDUTH, “The Voltaic Pile and Electro-Chemical Theory in 1800”, *Ambix*, 27 (1980), pp. 26-35.

<sup>13</sup> H. DAVY, *The Collected Works of Sir Humphry Davy*, 9 vols, J. DAVY, ed., (New York, 1972), II, pp. 155-63, on p. 162. For Davy’s views on electrochemistry and the action of the pile, see C. RUSSELL, “The Electrochemical Theory of Sir Humphry Davy”, *Annals of Science*, 15 (1959), pp. 1-13; and T.H. LEVERE, *Affinity and Matter: Elements of Chemical Philosophy 1800-1865*, (Oxford, 1971), pp. 25-59.

<sup>14</sup> J. RITTER, *Beyträge zur Nähern Kenntniss des Galvanismus und der Resultate seiner Untersuchung*, 2 vols., (Jena, 1800-5). W.D. WETZELS, *Johann Wilhelm Ritter: Physik im Wirkungsfeld der Deutschen Romantik*, (Berlin, 1973). For a careful study of Ritter, Pfaff, Humboldt and other German contributors to galvanic science, see M.J. TRUMPLER, *Questioning Nature: Experimental Investigations of Animal Electricity in Germany, 1791-1810*, thesis, (Yale University, 1992).

<sup>15</sup> Cited in W.D. WETZELS, “J.W. Ritter: Electrolysis with the Volta-Pile”, in DUPBERNELL and WESTBROOK, cit. 2, pp. 77-83, on p. 73.

evidence for his belief through studies of the oxidation of the metals in a voltaic pile. In Denmark, Hans Christian Ørsted, a close friend and admirer of Ritter, followed Ritter's chemical conception of the pile but without giving chemical action priority over the voltaic contact force. Ørsted tended to consider chemical effects and electricity as two manifestations of the same "powers".<sup>16</sup> Yet another of the early chemical pioneers was Georg Friedrich Parrot, a Finno-Russian scientist, who in 1802 attempted to explain voltaic electricity as a result of oxidation.<sup>17</sup>

By 1802 the contours of a new electrical controversy, this time concerning the action of the pile, were clearly visible. According to Volta's contact theory, the cause of the activity of the pile was the primitive electromotive force acting between two different metals; the result of the contact force might be chemical changes, but the force itself did not depend on such changes. The chemical theorists, on the other hand, argued that chemical processes played a much more central role and were the very cause of the pile's activity. Although the chemical view had many adherents in the early years of the century, in most countries the contact theory soon became generally accepted. In France, interest in the question was initially modest but in 1803 Jean Baptiste Biot wrote a detailed report in which he offered an electrostatic version of Volta's theory.<sup>18</sup> Although Biot's theory differed rather significantly from Volta's, it retained the contact force as the basic mechanism and denied any active role to oxidation processes. Biot's work was instrumental in turning almost all French scientists toward some kind of contact theory.

Also Davy, the eminent electrochemist and one of the pioneers of the chemical alternative, moved toward the contact orthodoxy. In 1807 he proposed a hybrid theory which gave chemical processes an important role but at the same time included Volta's notion of a metal-metal contact force causing the electrical fluid to enter a state of disequilibrium. He admitted that he had himself "to a certain extent adopted" the chemical theory, which "in the early stage of the investigation, appeared extremely probable", but now he felt that new experiments forced him to give up his earlier view.<sup>19</sup> Among Davy's arguments were the occurrence of electrical effects without any trace of chemical change, and, conversely, the occurrence of chemical changes without any detectable electrification. However, Davy recognized that the contact theory was unable to explain satisfactorily the closed electrical circuit and that chemical action could not be completely ignored. In

<sup>16</sup> H.C. ØRSTED, *Ansicht der Chemischen Naturgesetze*, (Berlin, 1812); reprinted in K. MEYER, ed., *H.C. Ørsted Scientific Papers*, (Copenhagen, 1920), pp. 35-169; and in English translation in K. JELVED, A. JACKSON, and O. KNUDSEN, eds., *Selected Scientific Works of Hans Christian Ørsted*, (Princeton, 1998), pp. 310-92.

<sup>17</sup> G.F. PARROT, "Skizze einer Theorie der galvanischen Electricität und der durch sie bewirkten Wasserzersetzung", [Gilbert's] *Annalen der Physik*, 12 (1803), pp. 49-73. OSTWALD, cit. 2, I, p. 418. PARTINGTON, cit. 1, IV, p. 133.

<sup>18</sup> T.M. BROWN, "The Electric Current in Early Nineteenth-Century French Physics", *Historical Studies in the Physical Sciences*, 1 (1969), pp. 61-103.

<sup>19</sup> DAVY, cit.13, V, p. 49.

his *Elements of Chemical Philosophy* of 1812, he pointed out that “It seems absolutely necessary for the exhibition of the powers of the Voltaic apparatus, that the fluid between the plates should be susceptible of chemical change”. Furthermore, he suggested that “The action of the chemical menstrea exposes continually new surfaces of metal; and the electrical equilibrium may be conceived in consequence, to be alternately destroyed and restored, the changes taking place in imperceptible portions of time”.<sup>20</sup>

| Mainly contact view          | Mainly chemical view       |
|------------------------------|----------------------------|
| A. Volta (1745-1827)         | G. Fabbioni (1782-1822)    |
| J.B. Biot (1774-1862)        | G.F. Parrot (1767-1852)    |
| R.J. Haüy (1743-1822)        | W.H. Wollaston (1766-1828) |
| M. van Marum (1750-1837)     | W. Nicholson (1753-1815)   |
| H. Davy* (1778-1829)         | W. Cruickshank (1745-1800) |
| L.W. Gilbert* (1769-1824)    | A.C. Becquerel (1788-1878) |
| J.J. Berzelius* (1779-1848)  | H.C. Ørsted (1777-1851)    |
| M.H. Jacobi (1801-1874)      | J.W. Ritter (1776-1810)    |
| C. Matteucci (1811-1874)     | M. Faraday (1791-1867)     |
| G. Zamboni (1776-1847)       | C.F. Schönbein (1799-1868) |
| C.H. Pfaff (1773-1852)       | A. de la Rive (1801-1873)  |
| G.F. Pohl (1788-1849)        | W. Ritchie (?-1837)        |
| S.G. Marianini (1790-1866)   | C. Pouillet (1791-1868)    |
| A. Bouchardat (1806-1886)    | P.M. Roget (1779-1869)     |
| G.T. Fechner (1801-1887)     | W.R. Grove (1811-1896)     |
| G.S. Ohm (1789-1854)         | C.J. Karsten (1782-1853)   |
| J.C. Poggendorff (1796-1877) | C.F. Mohr (1806-1879)      |
| G.G. Schmidt (1768-1837)     |                            |

**Table 1** Scientists involved in the voltaic controversy (1792-1845).

Davy’s 1807 conversion to a kind of contact theory illustrates the growing popularity of Volta’s view which a few years later came to obtain an almost paradigmatic status. The development of high-tension dry piles by Giuseppe Zamboni and others contributed to the acceptance of the contact theory; it seemed that such piles retained their electrical tension without any sign of chemical activity.<sup>21</sup> However, the chemical alternative was far from eradicated and in the

<sup>20</sup> Ibid., IV, pp. 122, 124. Much later, in 1826, Davy reaffirmed this point of view and concluded that the contact between metals cannot alone explain the action of the pile, *ibid.*, VI, pp. 305-43.

<sup>21</sup> The case of the dry pile is examined in W. HACKMANN, “The enigma of Volta’s ‘contact potential’ and the development of the ‘dry pile’”, forthcoming in this series.

1820s the controversy flared up again. During the period from 1792 to about 1845, a large number of Europe's chemists and physicists became involved in the controversy, in the sense that they either played active parts in it or, more commonly, held views that placed them (for a shorter or longer period) in one of the two rival camps.<sup>22</sup> The main figures in the protracted controversy are listed in the table above. Their positions vis-à-vis the pure contact theory and the pure chemical theory are impressionistically indicated by their locations in the table; the asterisks indicate the few cases where a scientist changed from one view to the other, namely, from the chemical to the contact view.

### 3. Chemical vs. Contact Explanations

By 1820 Volta's contact theory seemed to be almost universally accepted with only a few weak voices, such as that of Parrot, speaking out in favour of the chemical view. In a retrospective comment of 1829 Parrot deplored that there was, especially in Germany, "something of a propaganda campaign to spread this [Volta's] theory, of which C. H. Pfaff was the self-proclaimed champion". He claimed that "I was perhaps the only one who did not allow himself to be shaken even for a moment".<sup>23</sup> However, by that time the chemical theory had experienced a notable revival and the contact theory was now openly challenged in what turned out to be one of the most protracted and confused controversies in the history of the physical sciences. Although not the first to revolt against voltaic orthodoxy, Antoine-César Becquerel in Paris and Auguste de la Rive in Geneva were soon recognized to be the leading champions of the chemical theory in the 1820s and 1830s.

According to his own testimony, Becquerel originally supported Volta's theory but converted, first in 1824, to the view that "whenever there is a chemical, thermal or mechanical action there is development of electricity". However, his ideas about the voltaic pile differed from those of de la Rive whom he frequently criticized. Thus, Becquerel accepted as a matter of fact the existence of a contact force which acted as the cause of chemical action. In his *Traité expérimental de l'électricité et du magnétisme* he characterized his view as "intermediate between the viewpoints of the contact theory and the chemical theory" and added that "I have not completely renounced the contact theory".<sup>24</sup> Yet, although he admitted the contact force between metals he considered it to be of only secondary importance and found it vanished in a closed circuit. He tended to ascribe electrical currents to the actions

<sup>22</sup> For more details about this part of the controversy, see N. KIPNIS, "Debating the nature of voltaic electricity", forthcoming in this series.

<sup>23</sup> G.F. PARROT, "Lettre à MM. les rédacteurs des Annales de chimie et de physique, sur les phénomènes de la pile voltaïque", *Annales de chimie et de physique*, 42 (1829), pp. 45-66, on p. 47.

<sup>24</sup> A.C. BECQUEREL, *Traité expérimental de l'électricité et du magnétisme*, 6 vols., (Paris, 1834-40), II, p. 137.

of chemical affinities rather than to the contact force. For example, in his explanation of his acid-alkali cell (or “oxygen cell”), invented in 1829, he concluded that the electrical current was produced mainly by the combination of acid and alkali.

If Becquerel was a cautious, somewhat half-hearted supporter of the chemical theory, de la Rive advocated a much purer and uncompromising version of anti-Volta theory.<sup>25</sup> In a long series of papers, starting in 1825, he criticized the contact theory of the pile and in a sequence of papers from 1828, 1833 and 1836 entitled “Recherches sur la cause de l’électricité voltaïque” he put forward his chemical alternative. The French-Swiss scientist argued that experiments showed that chemical action was always a precondition for electrical phenomena and this fact, as he claimed it to be, spoke strongly against the contact theory. As he formulated it in 1836: “If two different bodies that are in contact are introduced into a liquid or a gas that exerts chemical action on one or both of them, then electricity is developed”. Contrariwise, in the absence of chemical action, “there is no development of electricity, at any rate not when thermal or mechanical action is absent”.<sup>26</sup> These two claims were the very opposite of what Davy had argued in 1807, when he abandoned the chemical theory. A large part of the controversy was concerned with what was fact and what was not. As to the many experiments, such as Volta’s, that showed pure contact electricity without chemical action, de la Rive’s favourite argument was to deny the complete absence of chemical processes. He typically and gratuitously suggested that there were in fact chemical processes involved that earlier researchers had failed to notice, namely between the metal and atmospheric oxygen or between the metal and small amounts of moisture. Like other actors in the controversy, de la Rive followed a double strategy by both criticizing his opponents’ claims and producing new experiments that supported his own view. For example, in one of his experiments he immersed gold and platinum in nitric acid, which reacts with neither of the noble metals. He noticed that no electrical current was produced, but when he added a few drops of hydrochloric acid the formed aqua regia attacked the gold, but not the platinum, and he now observed the production of a current. Similarly he showed that whereas platinum and palladium in dilute sulphuric acid were electrically passive, the addition of nitric acid produced a current. These results he considered to be in agreement with the chemical theory but inexplicable according to the contact theory.

De la Rive’s views were not accepted by the majority of electrical researchers who quickly produced counter evidence and counter arguments. Stefano Marianini, who had started his career in Pavia and in 1830 had become professor of physics in

<sup>25</sup> K.M. CANEVA, “La Rive, Arthur-Auguste de”, in *Dictionary of Scientific Biography*, (New York, 1973), VIII, pp. 35-7.

<sup>26</sup> A. DE LA RIVE, “Recherches sur la cause de l’électricité voltaïque”, *Mémoires de la société de physique et d’histoire naturelle de Genève*, 7:2 (1836), pp. 457-517; here quoted from OSTWALD, cit. 2, I, p. 445.



Modena, were among those who attacked the chemical theory of the Genevan physicist. In a paper of 1830 Marianini criticized – or deconstructed – de la Rive’s gold-platinum experiment and showed that it could not be taken as support for the chemical theory.<sup>27</sup> Moreover, he showed that this theory, in the form proposed by de la Rive, was unable to explain the fundamental fact of the voltaic pile, namely, that the voltage of many cells forming a pile is larger than the voltage of a single cell. When de la Rive published his theory of the pile six years later it did indeed (although this went unrecognised by de la Rive) lead to the obviously wrong result that only the extreme pairs of metals in a pile are active. Other criticism was launched by the French scientist Apollinaire Bouchardat who in 1834 reported experiments contradicting de la Rive’s ideas and concluded as follows: “The development of electricity precedes the chemical action. Chemical action is not the reason for the development of electricity. On the contrary, the energy of chemical action depends on the electric force developed due to the contact”.<sup>28</sup>

The most determined and dogmatic defender of voltaism was undoubtedly Christoph Heinrich Pfaff of the University of Kiel, a German-Danish veteran in galvanic and voltaic research. In his earliest work on the Volta pile, from 1802, he was inclined to the chemical view but he later changed his mind completely and became for the contact theory what de la Rive was for the chemical theory.<sup>29</sup> In 1814 Pfaff sharply criticized the chemical theories of the pile that Berzelius, Davy, Ritter and others had proposed.<sup>30</sup> Fifteen years later he launched his first attack against de la Rive, which included a repetition of Volta’s original condenser experiment, but now in vacuum (that is, low pressure) and in various dried gases. Since he obtained the same results as reported by Volta he felt justified in concluding that “it is impossible to assign any external and foreign circumstance, other than contact, as the cause for the electricity developed”.<sup>31</sup> De la Rive’s rather lame reply, included in his 1833 memoir, was that although he accepted Pfaff’s results there might still be

<sup>27</sup> S.G. MARIANINI, “Memoria sopra la teorica chimica degli elettromotori voltiani semplici e composti”, *Il poligrafo. Giornale di scienze, lettere, ed arti*, 3 (1830), pp. 79-106; from OSTWALD, cit. 2, I, p. 449.

<sup>28</sup> A. BOUCHARDAT, “Relations entre les actions électriques et les actions chimiques”, *Annales de chimie et de physique*, 53 (1834), pp. 284-304, on p. 304.

<sup>29</sup> H.R. WIEDEMANN, “Alessandro Volta e il fisico tedesco Christoph Heinrich Pfaff”, *Periodico della società storica comense*, 52 (1986-7), pp. 39-48. See also H. KRAGH and M. BAK, “Christoph H. Pfaff and the Controversy over Voltaic Electricity”, *Bulletin for the History of Chemistry*, 25 (2000), forthcoming. I have benefited from Bak’s Master thesis, M. BAK, *Christoph Heinrich Pfaff og Kontroversen om Voltasøjlen, 1828-1845*, (University of Aarhus, 1999).

<sup>30</sup> C.H. PFAFF, “Revision und Kritik der bisher zur Erklärung der galvanischen Erscheinungen aufgestellten Theorien [etc.]”, [Schweigger’s] *Journal für Chemie und Physik*, 10 (1814), pp. 179-200.

<sup>31</sup> C.H. PFAFF, “Défense de la théorie de Volta, relative à la production de l’électricité par le simple contact, contre les objections de M. le professeur A. de la Rive”, *Annales de chimie et de physique*, 41 (1829), pp. 236-47.

traces of oxygen in the vacuum, or the gases might contain small amounts of water vapour, and so the observed electrical tension might be the result of chemical effects. In order to demonstrate electricity without chemical action Pfaff also experimented with a zinc-copper Volta pile in which the metal pairs were separated by a saturated solution of zinc sulphate freed from dissolved air. According to the chemical theory one would suspect electrical passivity because zinc sulphate exerts no chemical action on either zinc or copper. Yet Pfaff found that a strong electrical action was produced, a result that de la Rive could not explain. What de la Rive could do, and what he did, was to explain it away.

Pfaff remained loyal to the contact cause and in 1837, more than thirty-five years after his first experiments with Volta's pile, he summarized the situation as seen from the voltaic point of view in a book entitled *Revision der Lehre vom Galvano-Voltaismus*.<sup>32</sup> As far as Pfaff was concerned nothing very important had happened in the theory of the pile since Volta's original work and he reconfirmed that this work must necessarily form the basis of any further progress. However, in spite of his repeated declarations of voltaic orthodoxy, Pfaff was now willing to consider, if only vaguely, the possibility of some kind of combination of the chemical theory and the contact theory. He speculated that perhaps the contact force, usually considered to be a primitive force with no need of explanation, could be understood in terms of the force of affinity associated with the electrical atmosphere surrounding the atoms. "Perhaps one cannot reject the view that the electromotive force may be caused by this affinity itself", he wrote, thus opening up a possible reconciliation of the two rival theories.<sup>33</sup> On the other hand, Pfaff seems not to have seriously considered such a reconciliation or synthesis. In experiments of 1841, he modified a Grove gas cell in such a way that there was no chemical action and thus, according to the chemical theory, no electricity could be produced. But Pfaff claimed to observe an appreciable electrical effect – "to my great joy, though not surprise, for I solidly rest on Volta's foundation".<sup>34</sup> This was one more variation on an old theme and one more example of an allegedly crucial experiment which was not crucial at all. As late as 1845, the then seventy-two-year-old scientist defended Volta's version of the contact theory and stressed that the contact force was a

<sup>32</sup> C.H. PFAFF, *Revision der Lehre vom Galvano-Voltaismus mit Besonderer Rücksicht auf Faraday's, de la Rive's, Becquerel's, Karsten's, u.a. Neuste Arbeiten über diesen Gegenstand*, (Altona, 1837).

<sup>33</sup> *Ibid.*, p. 226.

<sup>34</sup> C.H. PFAFF, "Ein experimentum crucis für die Richtigkeit der Contacttheorie der galvanischen Kette, und für die ökonomische Anwendbarkeit der Kette als bewegendes Princip durch Elektromagnetismus", [Poggendorff's] *Annalen der Physik und Chemie*, 53 (1841), pp. 303-9. Pfaff's paper was a response to C.F. SCHÖNBEIN, who considered the gas cell a vindication of the chemical theory (in his "Notizen über eine Volta'sche Säule von ungewöhnlicher Kraft", *ibid.*, 49 (1840), pp. 511-4).

primitive power that was neither in need of explanation nor restricted by the recently formulated law of force conservation.<sup>35</sup>

Pfaff was the most ardent champion of the contact theory, but he was far from alone in defending the true cause of voltaism. In Germany, a country where chemical heterodoxy found little sympathy, the contact theory was defended by Georg Simon Ohm, Georg Friedrich Pohl, Johann Christian Poggendorff and Gustav Theodor Fechner, among others. We cannot here deal with all their arguments and experiments; mentioning a few aspects must suffice. Pohl, a scientist inclined towards the views of the *Naturphilosophen*, is of some interest because he held ideas that were, in a sense, intermediate between the chemical and the contact theory. Although he criticized the chemical theory, and that of Becquerel in particular, his version of contact theory was far from the orthodox voltaic view associated with Pfaff. In 1826 he wrote that “So far contact electricity of the metallic parts has been considered as the proper driving force of the cell. ... [But I must conclude] that this driving force is nothing but the activity indicated by the contact electricity between the liquid and the metal”.<sup>36</sup> Also Ohm argued that metal-liquid contact was the essential source of electrical tension,<sup>37</sup> and in Italy Marianini held a similar view. To ascribe the electromotive force to contacts between metal and liquid was a major retreat from the pure form of voltaism, according to which contact between dissimilar metals was the only, or at least the dominant, source of electricity. (In defence of his view Ohm emphasized that Volta himself had made a similar suggestion). Marianini went even further and suggested that actual contact was not necessary, and that “contact” electricity could arise even between two dissimilar metals when separated by small intervals of air.<sup>38</sup>

Fechner, the physicist turned psychologist, was one of several contactists who believed they had delivered the chemical theory a mortal blow in the form of crucial experiments. In 1829 and more fully in 1837, he analysed and modified some of de la Rive’s experiments and arrived, expectedly, at conclusions diametrically opposed to those of de la Rive. One of his experiments, which he himself termed an *experimentum crucis*, consisted in a zinc-copper battery in water, with half the pairs of the plates opposed to the other half. Of course, no current was produced. When adding hydrochloric acid to one half of the battery he noted the expected development of hydrogen in this half and also the development of a current which, remarkably, went from the water cells to the acid cells. Moreover, he found that the cells with the acid, if isolated from the other cells, produced a far stronger current

<sup>35</sup> C.H. PFAFF, *Parallele der Chemischen Theorie und der Volta’sche Contacttheorie der Galvanischen Kette* [etc.], (Kiel, 1845). CANEVA, cit. 1, p. 183.

<sup>36</sup> G.F. POHL, *Der Process der Galvanischen Kette*, (Leipzig, 1826), p. viii.

<sup>37</sup> G.S. OHM, “Versuche über den elektrischen Zustand der einfachen galvanischen Kette [etc.]”, [Schweigger’s] *Journal für Chemie und Physik*, 63 (1831), pp. 160-89.

<sup>38</sup> S.G. MARIANINI, “Sulla teoria degli elettromotori [etc.]”, *Memorie di matematica e di fisica della società italiana delle scienze*, 21 (1837), pp. 205-46.

than the cells with the water. Whereas Fechner could readily explain the result on the basis of the contact theory, namely as a result of the increased conductivity of the liquid when the hydrochloric acid was added, “it is not at all clear to me how to explain the success of this experiment from the standpoint of the chemical theory”.<sup>39</sup> Alas, what Fechner believed to be a crucial experiment was not really a proof against the chemical theory and neither de la Rive nor other advocates of the chemical view found it particularly impressive. Like other allegedly crucial experiments in the controversy – and there were many of them – it failed to decide between the two rival theories.

The many attacks on the chemical theory, especially launched by German physicists, demonstrated the weakness of de la Rive’s theory without in any way refuting the chemical view, which continued to challenge the contact theory. There were phenomena that favoured the contact theory but then there were also phenomena that favoured the chemical theory. To the latter group belonged the experiments with gas cells that, in 1842, led to William Robert Grove’s invention of the hydrogen-oxygen battery. As far as Grove was concerned, his gas cell amounted to a refutation of the contact theory – one more crucial experiment. Although he asserted that he was “by no means wedded to any theory”, he concluded that “if there be any truth in the contact theory, I either misunderstand it or my mind is unconsciously biased”. He asked, rhetorically: “Where is the contact in this experiment, if not everywhere? Is it at the points of junction of the liquid, gas, and platina? ... Contact may be necessary, but how can it stand in the relation of a cause, or of a force?”<sup>40</sup> Although Grove found the gas cell contradicted the contact theory, of course defenders of this theory thought otherwise. Poggendorff, for one, readily came up with a contact-based explanation which, to his mind, was satisfactory. Moreover, he found Grove’s battery contradicted the chemical theory: “What grounds remain, then, for the so-called chemical theory? I find absolutely none! It appears to me that the inadequacy of this theory cannot be demonstrated in a more illuminating way than by the battery described above [by Grove]”.<sup>41</sup> Polarization phenomena, which became a central field of research from about 1835, proved easier to understand within the framework of the chemical theory than on the basis of the contact theory. By the late 1830s a chemically based explanation of polarization effects had been obtained by Christian Schönbein, Michael Faraday and others, whereas Ohm, Fechner, Poggendorff and their contactist allies faced great difficulties in coming up with an alternative explanation.

<sup>39</sup> G.T. FECHNER, “Rechtfertigung der Contact-Theorie der Galvanismus”, [Poggendorff’s] *Annalen der Physik und Chemie*, 42 (1837), pp. 481-516, on p. 515.

<sup>40</sup> W.R. GROVE, “On a Gaseous Voltaic Battery”, *Philosophical Magazine*, 21 (1842), pp. 417-20, on p. 420.

<sup>41</sup> Editor’s appendix to the German translation of Grove’s paper. [Poggendorff’s] *Annalen der Physik und Chemie*, 58 (1843), pp. 207-10, on p. 207.

The most important reason for the continual appeal of the chemical theory came, however, from another quarter, namely, Faraday's discovery of his electrolytic laws. In his famous paper of 1834 "On Electro-Chemical Decomposition", Faraday mentioned that "the definite production of electricity ... proves, I think, that the current of electricity in the voltaic pile is sustained by ... chemical action, and not by contact only".<sup>42</sup> And Faraday went further. As to "the great question of whether it [the electricity] is originally due to metallic contact or to chemical action", he reported experiments that proved, "in the most decisive manner, that *metallic contact is not necessary for the production of the voltaic current*".<sup>43</sup> Faraday was already predisposed toward the chemical theory and his belief was greatly strengthened by his new electrochemical discoveries. As the importance of Faraday's laws became recognized, the chemical cause gained strength. It was now possible to correlate proportionally the tension (or "intensity") of the pile with the chemical affinities involved and thereby answer a criticism often raised by the contact camp. This consequence of the electrochemical laws was pointed out by Faraday in 1834 and eagerly welcomed by the chemical theorists. It was repeated two years later by de la Rive, who stated that "The intensity of the currents developed in combinations and in decompositions is exactly proportional to the degree of affinity which subsists between the atoms whose combination or separation has given rise to these currents".<sup>44</sup>

Yet, although Faraday's discoveries were welcome ammunition for the advocates of the chemical theory, they did not make any of the contact theorists change their view. The case of Jöns Jacob Berzelius merits attention. The Swedish chemist had originally, in 1807, argued for a chemical explanation of Volta's pile, but later he inclined to support the contact theory. When he became acquainted with Faraday's laws he hesitated to accept their validity and did not consider them a strong argument against the contact theory.<sup>45</sup> In his influential textbook of chemistry, Berzelius argued against de la Rive and the chemical theory, which he found was contradicted by experiment. "The so-called chemical theory ... has been

<sup>42</sup> M. FARADAY, *Experimental Researches in Electricity*, 2 vols., (New York, 1965), par. 872. In this and other quotations from the book I leave out the paragraph numbers that Faraday included in the text.

<sup>43</sup> *Ibid.*, par. 878, 887.

<sup>44</sup> WHITTAKER, *cit.* 3, I, p. 181. A qualitative version of the rule had been formulated as early as 1829 by Peter Mark Roget, a British scientist and active supporter of the chemical theory. For the history of Faraday's laws, see S.M. GURALNICK, "The contexts of Faraday's electrochemical laws", *Isis*, 70 (1979), pp. 59-75.

<sup>45</sup> J.J. BERZELIUS, in his *Jahres-Bericht über die Fortschritte der Physischen Wissenschaften*, 15 (1836), pp. 30-9. See also C. RUSSELL, "The electrochemical theory of Berzelius", *Annals of Science*, 19 (1963), pp. 117-45.

completely refuted”, he wrote in 1843.<sup>46</sup> At that time the controversy was no less undecided and confused that it had been twenty years earlier.<sup>47</sup>

#### 4. Energy Conservation and the Voltaic Pile

Volta’s contact force was, by modern standards, a strange force. It was inexhaustible, an *elettro-motore perpetuo* capable of producing a never-ending current. In his letter to Banks of 1800, Volta admitted this feature of his theory without embarrassment. “This endless circulation of the electric fluid (this *perpetual motion*)”, he wrote, “may appear paradoxical and even inexplicable, but it is no less true and real; and you feel it, as I may say, with your hands”.<sup>48</sup> The apparent inexhaustibility of the contact force played no role in the controversy until the late 1830s, but it was noted by Peter Mark Roget in his work of 1829 as part of a criticism of the contact theory. After having noted that “all the other powers of nature” are subject to a principle of conservation, he wrote: “But the electromotive force ascribed by Volta to the metals when in contact is a force which, as long as a free course is allowed to the electricity it sets in motion, is never expended, and continues to be exerted with undiminished power, in the production of a never-ending effect. Against the truth of such a supposition the probabilities are all but infinite”.<sup>49</sup> Roget’s argument, based on an early anticipation of the principle of force conservation, would soon be repeated and amplified by Faraday in a full-scale attack on the contact theory.

In the summer of 1839, while preparing his long, seminal paper “On the Source of Power in the Voltaic Pile”, Faraday wrote in his diary that “By the great argument that no power can ever be evolved without the consumption of an equal amount of the same or some other power, there is *no creation of power*; but contact would be such a creation”.<sup>50</sup> Faraday now came out as an unreserved supporter of the chemical theory, declaring himself in line with de la Rive and “that admirable electrician” Becquerel, and launched what he believed was a devastating attack on the rival contact theory. Of course, this was merely a repetition of views he had stated six years earlier, but at that time to little avail. “For myself I am at present of the opinion which De la Rive holds”, he wrote, “and do not think that, in the voltaic

<sup>46</sup> J.J. BERZELIUS, *Lehrbuch der Chemie*, 5th ed., (Dresden, 1843), p. 87. In the 4th edition of 1835, Berzelius reviewed the controversy and declared himself in favour of the contact theory (pp. 127-31).

<sup>47</sup> For a contemporary review, see W. BEETZ, “Die Fortschritte des Galvanismus in den Jahren 1837-1847”, *Repertorium der Physik*, 8 (1849), pp. 1-351.

<sup>48</sup> Quoted in DIBNER, cit. 8, p. 124.

<sup>49</sup> ROGET’s work was reprinted in his *Treatises on Electricity, Galvanism, Magnetism, and Electro-Magnetism*, (London, 1832), from where Faraday quoted it in 1840. Here quoted from WHITTAKER, cit. 3, I, p. 182.

<sup>50</sup> L.P. WILLIAMS, *Michael Faraday: A Biography*, (New York, 1965), p. 367.

pile, mere contact does anything in the excitation of the current, except as it is preparatory to, and ends in, complete chemical action”.<sup>51</sup> Faraday’s weapons were powerful and diverse, consisting in part of methodological arguments, in part of a large number of experimental findings, and in part of arguments based on principles of natural philosophy. As to the experimental part of his essay, by far the longest part of it, he cited a wealth of data which either went against the contact theory or supported the chemical theory. These experimental arguments were impressive, but hardly decisive. In essence, Faraday claimed that there was complete correspondence between chemical and electrical activity and that this amounted to overwhelming evidence for the chemical theory. Specifically, among his conclusions were these: “2030. Chemical action does evolve electricity. 2031. Where chemical action has been, but diminishes or ceases, the electric current diminishes or ceases also. 2036. When the chemical action changes the current changes also. 2038. Where no chemical action occurs no current is produced. 2040. When the chemical action which either has or could have produced a current in one direction is reversed or undone, the current is reversed (or undone) also”.<sup>52</sup> However, the somewhat rash generalizations from the many experiments failed to convince contact supporters such as Pfaff, Fechner and Poggendorff. There was little that was new in the experiments and what was new they could explain, or explain away, by assuming contact potential between liquids or metals or by some other saving strategy. Moreover, they continued to produce new experiments which they believed contradicted Faraday’s generalizations.

What Faraday modestly called “a certain body of experimental evidence” was only part of his ammunition against the contact theory and not, in the long run, the most deadly part. The final section of Faraday’s paper, on “The Improbable Nature of the Assumed Contact Force”, dealt with the controversy from the point of view of general principles of natural philosophy and it was here that he made use of energetic arguments. He argued that the contact theory “virtually denies the great principle in natural philosophy, that cause and effect are equal”, and explained his claim as follows:

The contact theory assumes, in fact, that a force which is able to overcome powerful resistance ... can arise out of nothing. ... This would indeed be *a creation of power*, and is like no other force in nature. ... It should ever be remembered that the chemical theory sets out with a power the existence of which is pre-proved, and then follows its variations, rarely assuming anything which is not supported by some corresponding simple chemical fact. The contact theory sets out with an assumption, to which it adds others as the cases require, until at last the contact force, instead of being the firm unchangeable thing as first supposed by Volta, is as variable as chemical force itself. Were it otherwise than it is, and were the contact theory true, then, as it appears to me, the equality of cause and effect must be denied. Then would the perpetual motion also be

<sup>51</sup> FARADAY, cit. 42, par. 1801.

<sup>52</sup> The numbers refer to the paragraphs of FARADAY, *ibid.*, where the sentences appear in italics.

true; and it would not be at all difficult, upon the first given case of an electric current by contact alone, to produce an electro-magnetic arrangement, which, as to its principle, would go on producing mechanical effects for ever.<sup>53</sup>

Faraday briefly returned to the matter in 1843, disturbed by “several attacks, from Germany, Italy and Belgium, upon the chemical theory of the voltaic battery, and some of them upon experiments of mine”. He repeated his view and added that until the contact theorists were able to address the question satisfactorily “I shall feel very little inclined to attach much importance to facts which, though urged in favour of the contact theory, are found by the partisans of the chemical theory just as favourably to, and consistent with, their peculiar views”.<sup>54</sup>

Faraday advocated the principles of the unity and the convertibility of forces, which were not quite the same as the principle of energy (or force) conservation first expressed by Robert Mayer in 1842 and given its full formulation by Hermann von Helmholtz five years later. The immediate impact of Faraday’s work was limited and his arguments did nothing to change the balance of power between the chemists and the contactists. The case was the same with Mayer’s work, which at first was little noticed and at any rate did not refer to the voltaic controversy.

In his 1845 work mentioned above, Pfaff referred to both Faraday and Mayer, but without admitting that the new ideas jeopardized his beloved contact theory. One might expect that Faraday’s arguments and the growing recognition of the principle of energy conservation would have terminated the controversy in favour of the chemical view, as claimed by Pearce Williams in his biography of Faraday.<sup>55</sup> However, as we shall see, this was not the case. In his important essay on the discovery of the principle of energy conservation, Thomas Kuhn suggested that the dominance of the contact theory among German scientists might “account for the rather surprising way in which both Mayer and Helmholtz neglect the battery in their accounts of energy transformations”.<sup>56</sup> As far as Helmholtz’s work is concerned, this suggestion is doubly ill-founded. For one thing, as pointed out by Fabio Bevilacqua, Helmholtz seems not to have accepted Faraday’s argument that Volta’s view was in irremediable conflict with the law of energy conservation.<sup>57</sup> For

<sup>53</sup> Ibid., par. 2071-2073. In a footnote, Faraday mentioned Roget’s argument of 1829, which, he said, he had not known of earlier.

<sup>54</sup> Ibid., II, p. 276.

<sup>55</sup> According to Williams, with Faraday’s work “The contact theory had been dealt a mortal blow from which it never recovered. By 1850, with the acceptance of the principle of the conservation of energy, the contact theory was recognized as being, *a priori*, impossible and quietly forgotten” (WILLIAMS, cit. 50, p. 371).

<sup>56</sup> T.S. KUHN, “Energy conservation as an example of simultaneous discovery”, pp. 66-104, in his *The Essential Tension: Selected studies in Scientific Tradition and Change*, (Chicago, 1977), p. 73.

<sup>57</sup> F. BEVILACQUA, “Helmholtz’s *Ueber die Erhaltung der Kraft*”, in D. CAHAN, ed., *Hermann von Helmholtz and the Foundations of Nineteenth-Century Science*, (Berkeley, 1993), pp. 291-333, on p. 328. However, although Bevilacqua’s point is well taken it has the wrong address. Kuhn did



another thing, Helmholtz did not, in fact, neglect the battery. Far from it, in *Über die Erhaltung der Kraft* he gave a detailed discussion of batteries with and without polarization, and with or without chemical decomposition. Helmholtz admitted the existence of a contact force between metals but also recognized Faraday's "decisive opposition to the contact theory", or that the principle of energy conservation "directly contradict[s] the prevalent conception of this contact force when the necessity of the chemical process is not comprised in the concept".<sup>58</sup> However, by interpreting the contact force in terms of attractive and repulsive short range forces between charged particles, he satisfied himself that there need not be any contradiction between energy conservation and the contact theory. Helmholtz did not explicitly side with any of the parties in the controversy.

The acceptance of the law of energy conservation did not simply imply that the chemical theory now became universally accepted and the contact theory discarded. It did make the chemical theory considerably more popular, though, but this theory was unable to completely replace the contact theory, which therefore continued to be used and investigated by several researchers. In particular, the chemical theory could not explain the elementary voltaic phenomenon, the existence of a potential difference between two metals in contact such as proved in Volta's condenser experiment. Around 1850 the controversy was rapidly declining, not because consensus had been achieved but rather because scientists realized how pointless it would be to continue along a course that so far had brought no clarification. In 1849 Schönbein suggested that time was ripe for closing the confrontation between the two theories. He believed that some kind of a *via media* had to be followed, and proposed his own theory which borrowed elements from both the chemical and the contact theory.<sup>59</sup> Schönbein's theory attracted but little interest and during the 1850s the controversy went on at slow heat, apparently on its way to disappearing from the scientific journals.

## 5. Resurrection of the Contact Theory and Continued Confusion

British researchers had not taken much part in the controversy between contact and chemical theories. When they did intervene, as was the case with Roget and Faraday, they supported the chemical side. Yet the resurrection of the contact theory was the result of a British physicist, William Thomson, who in the 1850s had

not, in fact, state that Helmholtz accepted a contradiction between energy conservation and the theory of contact electrification.

<sup>58</sup> H. HELMHOLTZ, *Über die Erhaltung der Kraft*, in Ostwald's *Klassiker der Exakten Wissenschaften*, 1 (1907), p. 35. For Helmholtz's view on electrochemistry, see also H. KRAGH, "Between Physics and Chemistry: Helmholtz's Route to a Theory of Chemical Thermodynamics", in CAHAN, cit. 57, pp. 403-31.

<sup>59</sup> C.F. SCHÖNBEIN, "Ueber die chemische Theorie der Volta'schen Säule", [Poggendorff's] *Annalen der Physik und Chemie*, 78 (1849), pp. 289-306.

become interested in contact electricity. In 1862 he published a new version of the contact theory which was in many ways faithful to Volta's original theory. "For nearly two years I have felt quite sure that the proper explanation of voltaic action in the common voltaic arrangement is something very near Volta's, which fell into discredit because Volta or his followers neglected the principle of the conservation of force", he wrote.<sup>60</sup> According to Thomson, two metals in contact would produce a potential difference at their junction, whereas there would be no potential difference between the metals and the surrounding air. Importantly, he provided strong experimental support for the contact theory by direct measurement of the potential difference between zinc and copper forming a ring. Earlier measurements of potential differences, based on a method designed by Friedrich Kohlrausch, had been indirect and gave results that were not easily reproducible. Thomson's experiment confirmed the existence of a voltaic zinc-copper force (that is, potential difference) and moreover showed that it was nearly the same as the electromotive force of a Daniell cell. This suggested that the contact force was responsible for the generation of current in a cell and that there was no net potential difference between the metals and the electrolytic liquid. In England, Thomson's contact theory became generally accepted – "a new orthodoxy", according to Hong.<sup>61</sup> However, it shared with earlier contact theories its inability to account in a natural way for certain phenomena, among which was the observation that a cell's electromotive force usually depends on the kind of electrolyte in which the two metals are placed. This was an old problem and Thomson and his followers sought to solve it by reintroducing an old assumption, namely, the existence of a small chemically-caused metal-liquid electromotive force in addition to the "real" metal-metal force. When William Ayrton and John Perry in 1878 succeeded in measuring the metal-liquid potential difference it was taken to imply confirmation of Thomson's theory.<sup>62</sup>

In his *Treatise* of 1873 Maxwell expressed a view different from Thomson's, although not, strictly speaking, an anti-contact view. Maxwell argued that the contact force between two metals was negligible and "the greater part of Volta's electromotive force must be sought for, not at the junction of the two metals, but at one or both of the surfaces which separate the metals from the air or other medium

<sup>60</sup> W. THOMSON, "New proof of contact electricity", *Proceedings of the Literary and Philosophical Society of Manchester*, 2 (1862), pp. 176-8, on p. 176. Thomson's theory and the controversy it evoked is expertly discussed in S. HONG, "Controversy over Voltaic Contact Phenomena, 1862-1900", *Archive for History of Exact Sciences*, 47 (1994), pp. 233-89, which work I largely follow. See also S. ROSS, "The Story of Volta Potential", in DUPBERNELL and WESTBROOK, cit. 2, pp. 257-70; and L.H. FISHER and R.N. VARNEY, "Contact Potentials between Metals: History, Concepts, and Persistent Misconceptions", *American Journal of Physics*, 44 (1976), pp. 464-75.

<sup>61</sup> HONG, cit. 60, p. 233.

<sup>62</sup> W. AYRTON and J. PERRY, "Contact Theory of Voltaic Action", *Proceedings of the Royal Society*, 27 (1878), pp. 196-238.

which forms the third element of the circuit".<sup>63</sup> Unfortunately, it was not possible to measure the metal-air contact electromotive force and for a period Maxwell's suggestion remained an isolated remark. It was only in the 1880s that Maxwell's idea was further developed by Oliver Lodge and other Maxwellians, including Oliver Heaviside, John Henry Poynting, and John A. Fleming, who all opposed Thomson's contact theory. At the 1884 meeting of the British Association of the Advancement of Science, Lodge gave a detailed review of voltaic electricity in which he criticized Thomson and argued that the observed voltaic effects were really metal-air effects.<sup>64</sup> For example, the electromotive force of a Daniell cell was to be understood as the difference between the potential differences of zinc and air, and copper and air. This is not to say that Lodge denied the existence of a metal-metal contact force, which he found "undoubted", but he believed it was very small compared with the metal-liquid force. Lodge's address gave rise to a controversy which peaked in 1884-85 and in which Thomson's theory was defended by, among others, Perry, Ayrton, Peter Guthrie Tait, and Fleeming Jenkin. In France, Henri Pellat cautiously supported Thomson's view in a large number of experimental works.<sup>65</sup>

A central question in the new controversy concerned the existence of an electromotive force between metal and air. Does the Volta effect depend on the atmosphere surrounding the metal plates, or is it an absolute effect depending on contact alone? The question was of course to be decided experimentally, but experiments gave varying results, were disputed, or were for other reasons unable to give a clear answer. The same was the case with another possible crucial experiment, suggested by Lodge, namely, the determination of contact forces in a perfect vacuum. With no air there would be no metal-air electromotive force either and so, according to the Maxwell-Lodge theory, there would be no electromotive force at all. Experiments performed under a pressure of  $10^{-6}$  atmospheres showed no difference in the electromotive force from that measured in ordinary air, but Lodge defended his case by arguing that even such a low pressure was far from being a perfect vacuum. As in the earlier controversy, experiments were unable to settle the matter. Although the question of metal-air contact electricity remained undecided for at least two more decades, the intensity of the controversy soon diminished, not because one of the parties had been proved right but because most of the British physicists lost interest in it. They may have agreed with George Forbes according to whom the voltaic problem belonged to the same metaphysical

<sup>63</sup> J. CLERK MAXWELL, *A Treatise on Electricity and Magnetism*, 2 vols., (New York, 1954), I, p. 370.

<sup>64</sup> O. LODGE, "On the Seat of the Electromotive Forces in the Voltaic cell", *Report, British Association for the Advancement of Science*, (London, 1885), pp. 464-529, which is also a good source for the earlier conflict between contact and chemical views.

<sup>65</sup> E.g., H. PELLAT, "Mesure de la différence de potentiel vraie de deux métaux au contact", *Comptes rendus*, 104 (1887), pp. 1099-102.

category as the scholastic pseudo-problem of the number of angels that can stand on the point of a needle.<sup>66</sup> Yet, by the turn of the century Thomson and Lodge still defended their opposite views.<sup>67</sup>

It should be noted that the new, mostly British debate over contact electricity differed in important ways from the earlier controversy between chemical and contact theories. Whereas the latter was concerned also with the explanation of the voltaic cell's current-generating and electrolytic actions, the later debate was restricted to pure contact electricity, e.g., to cells with no open circuit and no generation of electrical current. Thomson's theory was indeed a revival of Volta's, but the Maxwell-Lodge theory was not a revival of the chemical theory and had almost nothing to do with the views of de la Rive or Faraday.<sup>68</sup>

Lodge considered it "quite false" to characterize the Volta contact force as a secondary effect caused by chemical processes and took pains to dissociate himself from the views of the Irish physicist J. Brown, who in 1878 concluded that the contact force was of chemical origin, possibly caused by films of air corroding the metal plates.<sup>69</sup> Nor did Lodge accept the "somewhat erratic" work of the Viennese physicist Franz Exner, who argued for a modern version of the chemical theory and denied the existence of true contact forces. In 1880 Exner wrote that the cause of "the production of electricity at the contact of two metals [lies], not in this contact, but in previous chemical actions of the surrounding media on the surfaces of the metals. ... so-called contact electricity is produced by the oxidation of the metal in contact by the oxygen of the air just as in galvanic cells it is evolved by oxidation of zinc".<sup>70</sup> Following a long tradition in the voltaic controversy, Exner's experimental proof was countered by other scientists more sympathetic to the contact theory. Thus Wsevolod von Uljanin, a Russian physicist working at the University of Strasbourg, reanalysed Exner's data and concluded that the experiment "not only does not provide a proof against the contact theory, but even provides a very beautiful [proof] for its correctness".<sup>71</sup>

As far as the chemists were concerned, by the turn of the century the concept of contact electricity was no longer interesting and not even worth contradicting.

<sup>66</sup> HONG, cit. 60, p. 264.

<sup>67</sup> W. THOMSON, "Contact Theory of Metals", *Philosophical Magazine*, 46 (1898), pp. 82-120. o. LODGE, "On the Controversy concerning Volta's Contact Force", *Proceedings of the Physical Society*, 17 (1900), pp. 369-430.

<sup>68</sup> PARTINGTON, cit. 1, IV, p. 701, incorrectly describes Lodge's theory as "chemical" and states that Lodge believed contact electricity to be due to oxidation processes. As made clear by Hong, Lodge's "potential chemical action" was not a real oxidation but the result of a "dielectric strain".

<sup>69</sup> J. BROWN, "Theory of Voltaic Action", *Philosophical Magazine*, 6 (1878), pp. 142-5. LODGE, cit. 64, p. 476.

<sup>70</sup> F. EXNER, "The Cause of the Production of Electricity by the Contact of Heterogeneous Metals", *Philosophical Magazine*, 10 (1880), pp. 280-95, on p. 280.

<sup>71</sup> W. VON ULJANIN, "Über ein auf die Contacttheorie bezüglichliches Experiment Exner's", *Annalen der Physik und Chemie*, 30 (1887), pp. 699-704, on p. 703.

Electrochemistry flourished and did well without it. There might exist contact potential between metals, but if so it was entirely inappreciable. According to Ostwald, writing in 1896, the first breakthrough towards a satisfactory solution of the century-old problem came with Helmholtz's works on double layers of 1879 and on the electromotive force of cells of 1882-83.<sup>72</sup> The latter theory, which was brought to perfection with Walther Nernst's celebrated 1888 theory of the cell, essentially solved all problems. But unfortunately Helmholtz did not himself draw correct conclusions from his work. "It must be admitted that to the end of his life [1894] Helmholtz appears to have been a supporter of the voltaic theory", Ostwald wrote, disapprovingly. "He regarded the great potential differences between metals obtained by the condenser method as real".<sup>73</sup> Building on Helmholtz's theoretical and experimental work, Ostwald concluded in 1887 that there is no significant potential difference between metals and that the source of a cell's potential difference is to be found in ionic processes in the electrical double layer between electrolyte and metal.<sup>74</sup> With the works of Ostwald and Nernst, two of the cornerstones of the successful ionic school of physical chemistry, most chemists considered the chemical theory vindicated and the voltaic problem solved. "The chemical theory has fought its way back", Ostwald asserted, and the result was "final victory".<sup>75</sup>

Some physicists thought otherwise and although, in a social sense, the controversy had largely disappeared by 1910 there was no consensus on the question of whether or not contact potentials exist as an intrinsic property of metals. About 1915 new life was brought to the half-forgotten contact theory from high-vacuum experiments on thermionic effects, photoelectricity and metal vapours. Among the physicists who argued in favour of contact potential were Irving Langmuir, Robert Millikan, and Owen Richardson, all future Nobel prize laureates. After having noted "the abandonment of the contact theory of electromotive forces by electrochemists", Langmuir concluded in a review paper of 1916 that "Within the last years very remarkable work in physics has demonstrated that contact potentials of large magnitude do exist, even between pure metals in a practically perfect vacuum".<sup>76</sup> The contact theory eventually came to be interpreted in terms of the electron affinity, a concept related to the work function which is again a measure of

<sup>72</sup> See KRAGH, cit. 58; and W. NERNST, "Die elektrochemischen Arbeiten von Helmholtz", *Die Naturwissenschaften*, 9 (1921), pp. 699-702.

<sup>73</sup> OSTWALD, cit. 2, II, p. 1009.

<sup>74</sup> W. OSTWALD, "Studien zur Contactelectricität", *Zeitschrift für Physikalische Chemie*, 1 (1887), pp. 583-610.

<sup>75</sup> OSTWALD, cit. 2, I, p. 289. However, Ostwald realized that "Even now there is an appreciable number of supporters of the contact theory", *ibid.* p. 694.

<sup>76</sup> I. LANGMUIR, "The Relation between Contact Potentials and Electrochemical Action", *Transactions of the American Electrochemical Society*, 29 (1916), pp. 125-180, reprinted in I. LANGMUIR, *The Collected Works of Irving Langmuir*, 12 vols., (Oxford, 1960-2), III, pp. 173-217, on p. 216.

the energy it takes to remove an electron from the surface of a metal in vacuum. The contact potential difference is given by  $eV_{ab} = F_a - F_b$ , where  $F_a$ ,  $F_b$  are work functions and  $e$  denotes the electron's charge. According to modern knowledge, then, the contact force is real and far from negligible. In this sense Volta's more than two-centuries old theory may be said to be true. On the other hand, this does not mean that the chemical theory is necessarily wrong. In a review of 1928, Alfred Porter concluded that the situation was still unsatisfactory. "It is still necessary to be cautious and to avoid dogmatism on this question", he wrote. "Much more detailed experimental knowledge is required before the electric circuit is really understood". He suggested a *via media*:

My own opinion is that, though the voltage at the metal-metal junction is likely to be much larger than the chemical school demanded, there is nothing to justify one in going to the opposite extreme and expecting that the *whole* of the electromotive of a circuit is located at that junction. Opposing schools may both take comfort in the thought that in some respects they are both right.<sup>77</sup>

Fourteen years later, Alan Chalmers, another British physicist, re-examined both viewpoints in a careful study and concluded that "the phenomena of the Volta effect can be given a consistent interpretation in terms either of the external potential differences, agreeing with the contact theory, or of the internal potential differences, agreeing with the chemical theory".<sup>78</sup> Following the conclusions of Porter and Chalmers one may be tempted to ask if the whole controversy was not just – much ado about nothing?

## 6. Perspectives and Conclusions

The controversy over explanations of the voltaic cell is one more contribution to the long list of controversies in the history of the physical sciences, but it is more than that. It is, in some respects, unusual, among other reasons because of its very long duration, its lack of clean resolution, and its involvement of a large number of both chemists and physicists. Contrary to most other controversies (such as that between Galvani and Volta) this one was not primarily between two individuals but included a relatively large part of the period's scientific community. Of course, some scientists – de la Rive and Pfaff in particular – were more prominent in the controversy than others, but it was far from limited to these combatants.

The first phase in the controversy was between a chemical and a physical (contact) explanation of the battery and so one might believe that it included a clear

<sup>77</sup> A.W. PORTER, "The Volta Effect", in *Report, British Association for the Advancement of Science*, (London, 1929), pp. 21-34, on p. 33.

<sup>78</sup> J.A. CHALMERS, "Contact Potentials", *Philosophical Magazine*, 33 (1942), pp. 399-430, pp. 496-513, pp. 599-613, on p. 429. I have not looked systematically into the later literature on the subject.

disciplinary component, with chemists defending the first kind of theory and physicists the second kind. However, one should not read too much into the term “chemical” theory. For one thing, in the early years of the nineteenth century the distinction between physics and chemistry was far from clear cut. It was only during the following decades that practitioners of chemistry and physics became increasingly self-conscious about the identification of their disciplines.<sup>79</sup> Although the majority of the contactists were physicists there were also chemists defending Volta’s theory. As mentioned, Davy and Berzelius were closer to the contact view than the chemical view; and the main protagonists of the chemical theory, Becquerel, de la Rive, and Faraday, were primarily physicists rather than chemists. Generally speaking, from the 1820s the controversy seems to have received much more interest in physics journals than in chemistry ones, and the later controversy over contact electricity was almost entirely an affair limited to the physics community.

Controversy studies have become increasingly popular during the last couple of decades and the one dealing with voltaic phenomena shows features that may well be of interest also to a more general understanding of the mechanism of scientific controversies.<sup>80</sup> Although it was a controversy based in disagreement over theory, it was definitely also a controversy of fact, that is, one in which the scientists disagreed about experiments and whether effects existed or not. Methodological arguments played some role in the nineteenth-century controversy, but neither a simple nor a decisive one. Occam’s razor and reasons of simplicity were often considered to favour the contact theory, but in the 1840s Faraday and others accused this theory of violating the rules of natural philosophy. I doubt if the controversy can be “rationally explained” within any of the existing frameworks of philosophy of science. On the other hand, it includes elements that may serve to illustrate important features in the scientific process and may, if properly researched, be

<sup>79</sup> On the relationship between physics and chemistry in the nineteenth century, see M.J. NYE, “Physics and Chemistry: Commensurate or Incommensurate Sciences?”, in M.J. NYE, J. RICHARDS, and R. STUEWER, eds., *The Invention of Physical Science*, (Boston, 1992), pp. 205-24; and E.N. HIEBERT, “Discipline Identification in Chemistry and Physics”, *Science in Context*, 9 (1996), pp. 93-119. For the early period, see also S. STRICTLAND, “Galvanic Disciplines: The Boundaries, Objects, and Identities of Experimental Science in the Era of Romanticism”, *History of Science*, 33 (1995), pp. 449-65.

<sup>80</sup> H.T. ENGELHARDT and A.L. CAPLAN, eds., *Scientific Controversies: Case Studies in the Resolution and Closure of Disputes in Science and Technology*, (Cambridge, 1987). R.G.A. DOLBY, “Controversy and Consensus in the Growth of Scientific Knowledge”, *Nature and System*, 2 (1980), pp. 199-218. For an analysis of controversies, especially in the history of chemistry, and references to the extensive literature, see also H. KRAGH, “S.M. Jørgensen and his Controversy with A. Werner: A Reconsideration”, *British Journal for the History of Science*, 30 (1997), pp. 203-19.

turned into a case-study no less valuable than Marcello Pera's study of the Galvani-Volta controversy.<sup>81</sup>

The case is instructive from the point of view of theory-experiment relationship, a focal problem in the philosophy of science. It is a useful reminder of the sometimes limited power of experiments in resolving scientific disputes. Perhaps the most striking feature of, in particular, the early phase of the controversy was the inefficiency of the hundreds of experiments with regard to deciding between the chemical and the contact view. The two groups largely agreed on what kinds of experimental results would settle the matter, such as results that unequivocally showed electrical action without chemical change (pro contact) or the absence of contact electrical action in vacuum or other non-chemical environments (anti contact). But if an experiment was claimed to contradict one of the theories ( $X$ , for short), what happened was not that  $X$  was rejected as wrong, but typically that the  $X$  protagonists denied the conclusion in one or more of the following ways. They could produce new experiments that contradicted  $X$  and supported their own theory,  $Y$ , and claim that these were more important. They could deny the validity of the experiment, i.e., argue that the alleged effects did not exist. If they had to accept the experiment, for instance if they got the same results by repeating it, they could deny that the results were theoretically relevant, argue that they were due to other effects, or introduce ad hoc modifications to protect the theory.

All these and other strategies were routinely used by both parties in the controversy, which offers numerous examples of how to protect a theory from falsification. It was quite common that scientists of different inclinations drew opposite conclusions from the very same experimental findings. They might agree that the experiment was crucial, but disagree about what it crucially refuted or confirmed.<sup>82</sup> The many crucial experiments turned out to be anything but crucial, and the entire episode may be taken to illustrate the view, held by some philosophers, that there do not exist crucial experiments except in textbooks on the philosophy of science.<sup>83</sup> Social constructivists may tend to see in the case a forceful demonstration of one of their favourite theses, that "all experimental findings may be criticized, and no experimental finding need be taken as a crucial confirmation or

<sup>81</sup> PERA, cit. 4; and M. PERA, "Radical Theory Change and Observational Equivalence: The Galvani-Volta Controversy", in W.R. SHEA, ed., *Revolutions in Science: Their Meaning and Relevance*, (Canton Mass., 1988), pp. 133-56.

<sup>82</sup> This was not a peculiarity of the chemical-versus-contact controversy, but can be found also in, e.g., the contemporary dispute concerning the existence of animal electricity. Thus PERA, cit. 4, p. 174, refers to how Leopold Nobili and Carlo Matteucci arrived at opposite conclusions from the same observation of a frog's electrical effect.

<sup>83</sup> I. LAKATOS, "The Role of Crucial Experiments in Science", *Studies in the History and Philosophy of Science*, 4 (1974), pp. 309-25.



disconfirmation of a theory it is said to test".<sup>84</sup> However, in my view it would be incorrect to draw from the voltaic controversy the conclusion that experiments are unable to decide between opposing theories. What the story of contact electricity shows is rather that it can be very difficult to reach consensus when the quantities involved are small, unstable, and difficult to measure reliably. It took a long time until contact potential could be measured accurately and reliably, but in the 1950s new experimental techniques solved the problem and finally resolved whatever was still left of the old controversy.<sup>85</sup>

<sup>84</sup> H. COLLINS and S. SHAPIN, "The Historical Role of the Experiment", in F. BEVILACQUA and P.J. KENNEDY, eds., *Using History of Physics in Innovative Physics Education*, (Pavia, 1983), pp. 282-92, on p. 285.

<sup>85</sup> P.A. ANDERSON, "A Direct Comparison of the Kelvin and Electron Beam Methods of Contact Potential Measurement", *Physical Review*, 88 (1952), pp. 655-8.