CHRISTOPH H. PFAFF AND THE CONTROVERSY OVER VOLTAIC ELECTRICITY

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Introduction

It has been 200 years since Alessandro Volta invented his famous pile, the first electric battery, and thereby

created an important starting point not only for the sciences of electricity and magnetism but also for the later electrical technology that so thoroughly has transformed society. The electric age in which we still live can reasonably be traced back to Volta's discovery. His pile immediately became the subject of intense scientific investigation, which included theoretical ideas of the origin of the electrical tension that seemed to occur spontaneously if only two different metals were brought in contact. This question figured prominently in the science of the first half of the nineteenth century, and it occupied physicists and chemists alike. Indeed, at that time the separation between physics and chemistry had not vet become manifest.

Figure 1. Chr. H. Pfaff (1773-1852). From C. Schmidt-Schönbeck, 300 Jahre Physik und Astronomie an der Kieler Universität, Verlag F. Hirt. Kiel, 1965, 216.

In a letter of October 30, 1801 to the Dutch scientist Martinus van Marum, Volta referred to "a highly esteemed German scientist, a zealous cultivator of physics, natural history, and chemistry, and the author of

works that are much to his honor (1)." The subject of Volta's praise was Christoph Heinrich Pfaff, a 28-year-old German chemist and physicist with whom Volta had recently become acquainted. Pfaff was already an en-

thusiastic expert in galvanic science, a field of study he cultivated throughout his long career. His many contributions to animal electricity and, in particular, the understanding of Volta's pile made him a key figure in Wilhelm Ostwald's massive 1896 history of electrochemistry. According to Ostwald, Pfaff was a "painstaking historian of galvanism and zealous defender of voltaism" who "won special merit particularly in the propagation of the knowledge of galvanic phenomena in Germany (2)." In addition to his numerous works in electrochemistry and inorganic analysis, the versatile Pfaff published many papers and books on subjects of physics, medicine, meteorology, botany, and pharmacy. He seems to have known most scientists in Europe and cor-

responded or had personal relations with important scientists and scholars such as Cuvier, Gay-Lussac, Dumas, Lichtenberg, Gmelin, Ørsted, Volta, Berthollet, Thénard,

Lagrange, Berzelius, Liebig, Faraday, Mayer, and Goethe.

Although he was a central figure in the scientific life of his time, today Pfaff is largely forgotten or relegated to footnotes in works on the history of science. This is probably because he made no significant discoveries, but rather made an impact as a teacher and propagator of science and through his many books, reviews, and papers. There is indeed a Pfaff included in the Dictionary of Scientific Biography, but he is Johann Friedrich Pfaff, a mathematician and Christoph's older brother. Curiously, when Chr. H. Pfaff does turn up in bibliographies and historical writings, his first name is often given as Christian rather than Christoph. For example, this is how he is named in the 1863 edition of Poggendorff's authoritative bio-bibliography, in the British Museum General Catalogue of Printed Books (1963), and also in the classical historical works of Edmund Whittaker and James Partington. Yet his first name was Christoph, such as proved by his autobiography (3).

Life and Career

Born on March 2, 1773 in Stuttgart, young Pfaff entered in 1782 the nearby Karl Academy, named after Württemberg's Duke Karl Eugen. He soon became fascinated by the scientific subjects that were taught at the Academy in addition to the classical languages. His early knowledge of chemistry mostly stemmed from Friedrich Gren's Systematisches Handbuch der Gesammten Chemie (1787-1790), which he studied by himself. Among his fellow students was the Frenchman Georges Cuvier, four years older, who would later become such a famous pioneer of zoology and paleontology. The close and, in the spirit of the time, romantic friendship with Cuvier became a turning point in Pfaff's life and reinforced his decision to devote his life to science. Cuvier became not only his friend but also his mentor and teacher. When Cuvier returned to Paris, he kept Pfaff regularly informed of Lavoisier's latest works and the ongoing revolution in chemistry (4). As a result, Pfaff, who had originally accepted the phlogiston theory, converted to the antiphlogistic doctrines and became an advocate of the new chemistry and its transfer to German soil (5).

Pfaff completed his medical studies at the Karl Academy with a Latin dissertation on animal electricity (*De Electricitate Sic Dicta Animali*) which in 1795 appeared in an extended and revised German edition (6).

It won him much praise and caught the attention of Volta, among others. After further studies in chemistry, physics and medicine he obtained in 1798 a chair at the Christian-Albrecht University in Kiel. He spent most of the year of 1801 in Paris, and it was here he met Volta and witnessed the Italian scientist's famous demonstration of the pile in front of Napoleon and other luminaries. Pfaff was fascinated by Volta and his marvelous apparatus and immediately took up his own experiments (7). In 1802 the ambitious young scientist wrote to van Marum (8):

I am working at present on a complete treatise on galvanism, in which I shall assemble in systematic order all the really authentic facts, and in which I shall reduce them to the laws of electricity.

Volta knew about Pfaff's project, of which he approved. On January 23, 1802, he wrote to Pfaff (9):

I am very much pleased with your idea of publishing a treatise which presents everything that has taken place concerning galvanism, and to put this matter in the clearest light; no one else can do it better than you. The works that you have done several years ago, [and] the order and method that govern them, prove it.

Although Pfaff's "complete treatise" never materialized, his work earned him a reputation as one of Europe's foremost specialists in electrochemistry and galvanism. Ludwig Gilbert, the German physicist and editor of *Annalen der Physik*, wrote that Pfaff (10):

...had worked meticulously in the new field of physics [and] with such excellent results that Volta, whom he met in Paris, entrusted him with advertising and cultivating his theory in Germany; ... [Pfaff's] article in the tenth volume of my *Annalen der Physik* (the year 1802, pp 219 and 121) still belongs to the most instructive accounts of the theory.

From 1801 to the end of his life in 1852, Pfaff investigated the action of the pile, defended Volta's notion of a metallic contact force, and wrote widely about voltaic phenomena. He was considered an international authority on the subject, which he surveyed in 622 pages for the new edition of Johann Gehler's *Physikalisches Wörterbuch*. Ostwald later praised the survey for Pfaff's "commendable care and thought (11)."

Yet galvanic and voltaic phenomena were only part of what Pfaff was concerned with during his busy scientific life. He was greatly interested in electromagnetism on which topic he wrote an early "history (12)," and in 1829 he learned from Faraday himself about the new way to produce electricity by means of induction.

Methodologically, Pfaff favored a positivistic view of science and never tired of emphasizing that chemistry and physics were solidly founded on experimentally established facts. He had no patience for the German Naturphilosophie and neither did he like Goethe's revolt against Newtonian science. Having read Goethe's Farbenlehre, he quickly responded with an anti-Goethe tract repudiating the views of the famous poet and heterodox amateur scientist (13). Much of Pfaff's time was occupied with medicine and pharmacy, and he also contributed significantly to analytical chemistry. He developed analytical techniques and wrote in the early 1820s a practically oriented handbook of analytical chemistry (14), according to William Brock the "first major ana-

chemists and pharmacists. In 1843, on the occassion of his 50-year's doctoral jubilee, the Danish king conferred upon him the title of *konferensraad* (Conference Councillor), a great honor and a recognition of his services to Danish science and culture. During the last years of his life, Pfaff lost his eyesight and was unable to work in his laboratory. He died on April 23, 1852 in his beloved Kiel, where he is buried.

Polemics I: Pfaff versus De la Rive

According to Volta, the action of the pile was due solely to a contact force (a *forze motrice*, or electromotive force) arising between two different metals, and not to

Table I. Chronology of Chr. H. Pfaff

1773 Born in Stuttgart, Germany.

1782 Enters Karl Academy.

1793 Doctoral dissertation (M.D.) on animal electricity.

1798 Professor (extraordinarius) at Kiel University, Medical Faculty.

1801 Studies in Paris. Meets Volta.

1802 Full Professor in chemistry and physics.

1804 Member of the Royal Danish Academy of Science.

1812 Corresponding member of the Berlin Academy of Sciences.

1828 Director of the Schleswig-Holstein Sanitation Board.

1829 Visit in Paris U. Gay-Lussac; J. B. Dumas) and London (W. Prout; M.Faraday).

1830 President of the physics-chemistry section of the (German) Society of Physicians and Natural Scientists.

1831 Chief editor of the Schleswig-Holstein pharmacopoeia.

1837 All-out rejection of chemical theory (Revision).

1838 Grand European tour.

1845 Last major work (Parallele). Resigns from Chair.

1852 Death.

1853 Publication of his autobiography (Lebenseritmerungen).

lytical textbook (15)." Among his few contributions to organic chemistry was an investigation, together with Liebig, of the chemical composition of caffeine (16). At the same time he did research in mineralogy, the composition of mineral waters, and technical chemistry (including the production of acetic acid and sulfuric acid) — to mention only some of his areas of work.

During the first half of the nineteenth century (until 1864) Kiel, the capital of Holstein, was part of the Danish Empire. Pfaff was often in Copenhagen and had close connections with H. C. Ørsted and other Danish

chemical processes of any sort. This view was reflected in the title of Volta's famous letter to Joseph Banks of March 20, 1800, namely, "On the Electricity Excited by the Mere Contact of Conducting Substances of Different Kinds (17)." Other scientists, among them Giovanni Fabbroni, Davy, and Berzelius, questioned the contact theory and suggested that the pile was in reality a chemical machine. According to the chemical theory, chemical changes were necessary for the production in the pile of an electrical tension or, if the circuit was closed, a current. This was the beginning of an unusually long and complex controversy that lasted for more than half

a century and involved many of Europe's finest chemists and physicists (18).

The voltaic pile was constructed from a large number of similar units connected in series, generally referred to as "galvanic" or "voltaic" elements. These much used and well known elements were composed of two dissimilar metals and a "moist conductor" that could be any kind of liquid or solution. Most of the numerous experiments conducted during the controversy were made with these galvanic elements rather than the voltaic pile, since one element conveniently constituted an adequate representation of the pile itself.

Pfaff was a self-proclaimed champion of the contact theory and considered himself a guardian of Volta's

views. In 1814 he launched an attack on the chemical theories proposed by Davy, Berzelius and others; and fifteen years later he was again on the warpath against what he saw as chemical heresy. The principal reason was a series of papers written by the Geneva scientist Auguste De la Rive that amounted to a fully developed chemical alternative to the contact theory. Another advocate of the chemical theory, the Paris physicist Antoine-César Becquerel, was somewhat more cautious and admitted the existence of a metallic contact force, although he considered it to be of secondary importance only. Based on a large number of experiments, De la Rive argued from 1825 onward that chemical change was invariably a precondition for voltaic phenomena, whereas, in the absence of chemical action, "there is no development of electricity, at any rate not when thermal or mechanical action is absent (19)." To De la Rive, this proved that the contact theory was wrong. To Pfaff, it proved that De la Rive was wrong. Pfaff's campaign against Becquerel, De la Rive, and other adherents of the chemical alternative included a modified repetition of Volta's fundamental condenser experiment, performed in vacuum or in various dried gases. Since he obtained the same result as reported by Volta, an electrical ten-

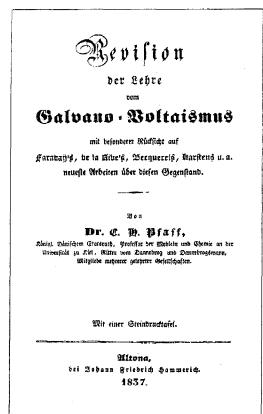


Figure 2. Title page of Pfaff's major work in the voltaic controversy.

sion, he concluded that "it is impossible to assign any external and foreign circumstance, other than the contact, as the cause for the electricity developed (20)." In order to demonstrate the production of electrical effects without chemical action, Pfaff also experimented with a zinc-copper galvanic element in which the metal pairs were separated by a saturated solution of zinc sulfate carefully freed from dissolved air. According to the chemical theory one would suspect the system to be electrically inactive because zinc sulfate exerts no chemical action on either zinc or copper. Yet Pfaff found that a strong electrical effect was produced, a result that left De la Rive puzzled. Pfaff measured the electrical effect both with a condenser and an electroscope (static or tension electricity), and with a galvanometer (dynamic or current electricity). Moreover, he challenged the "chemists" to explain why the tension of the pile increases with the number of couples.

Pfaff remained loyal to the contact cause, battling not only his chief opponent De la Rive but also other

chemical theorists, including Becquerel France, Michael Faraday in England, and Christian Schönbein and Friedrich Mohr in Germany. In 1837 he summarized his work on "galvano-voltaism" during more than two decades in a book that he believed would settle the matter in favor of Volta's theory (21). He was mistaken. On the con-

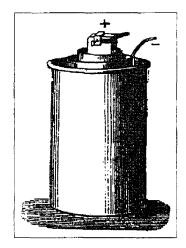


Figure 3. The cylinder-type cell, or galvanic element,, was frequently used in the voltaic controversy. Illustration from A.-C. Becquerel and E. Becquerel, Traité d'Électricité et de Magnétism, Libraire de Firmin Frères, Paris, 1855, vol. 1, 231.

trary, at that time the chemical theory gained strength, in part because of Faraday's entrance in the debate. Becquerel and De la Rive continued to defend the chemical theory. Citing "thousands of experiments," Becquerel concluded in a textbook of 1842 that "the electricity released by the pile totally originates from the chemical action (22)."

It should be noted that although Pfaff was undoubtedly the most energetic and persistent advocate of the contact theory, he was far from alone in his criticism of the chemical alternative. In the 1830s he was followed by several other scientists, both chemists and physicists; and for a period the contact theory was generally believed to be a better explanation of the pile than the chemical theory. Among the German scientists who defended the contact theory were Georg S. Ohm, Johann C. Poggendorff, Gustav T. Fechner, and Georg F. Pohl.

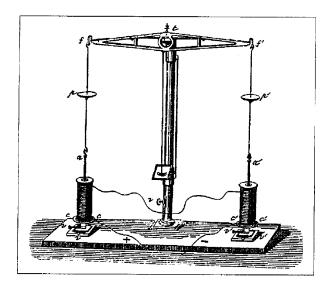


Figure 4. An electromagnetic balance. The cells were connected to wires wound up around iron cores, in this way creating an electromagnet varying in strength according to the strength of the current. The electromagnet would attract the pans of the balance and thus enable a measurement of the current intensity in terms of weight. Illustration from A.-C. Becquerel and E. Becquerel, Traité d'Électricité et de Magnétism, Libraire de Firmin Frères, Paris, 1855, vol. 1, 231.

An Indecisive Experiment: Grove's Cell

In 1839 William Grove, the British physicist and inventor of the fuel cell (also in 1839), constructed a cell of remarkable strength. His element consisted of a zinc electrode in a dilute solution of sulfuric acid and a plati-

num electrode immersed in nitric acid. The two liquids were separated by a porous wall. Together with his friend Schönbein, the famous discoverer of ozone and a longtime defender of the chemical theory, Grove performed in his London laboratory a number of experiments with the new galvanic element. The two scientists observed a considerable "chemical action" of the acid on the zinc plate, that is, the zinc corroded visibly because of the acid. Schönbein concluded that the powerful chemical action was connected with the equally powerful effects of the element, and that the cell was therefore a convincing argument in favor of the chemical theory (23). Pfaff, of course, disagreed. He decided to repeat the experiment and had his own design of Grove's cell made in Copenhagen. His version consisted of a central zinc rod within a porous clay cylinder surrounded by a platinized porcelain cylinder (Fig. 3). With this cell Pfaff repeated the experiments made by Grove and Schönbein. He measured the power (Kraft) of the cell by means of an electromagnetic balance and found the very large carrying capacity of 40 pounds (Fig. 4). He then exchanged the sulfuric acid with an amount of zinc sulfate dissolved in water, that is, a solution incapable of exerting chemical action on zinc. The carrying capacity now measured 50 pounds.

The results made Pfaff note that (24):

To my great joy, though not surprise, for I firmly stand on voltaic ground, I found that the power was enhanced.

In a letter to his friend H. C. Ørsted, he wrote (25):

I hasten to inform you of an experiment entirely decisive for the theory of voltaism, definitively silencing the long fought struggle over the source of electricity in the closed [galvanic] chain, and completely ensuring the triumph of the contact theory.

The interpretation seemed obvious to Pfaff, who rhetorically asked his colleague in Copenhagen (25):

Could there be a more vindictive proof of the contact theory and against the chemical theory?

However, the experiments with the Grove cell were no more decisive than any other of the so-called crucial experiments that were so common in the controversy.

Polemics II: Pfaff versus Faraday

Michael Faraday's electrochemical works were another challenge to the contact theory. Even before 1834, the year when he announced his electrolytic laws, Faraday was predisposed toward the chemical theory; and his electrochemical discoveries strengthened him in his belief. He addressed "the great question of whether it [the electricity] is originally due to metallic contact or to chemical action" and reported experiments that proved "in the most decisive manner, that metallic contact is not necessary for the production of the voltaic current (26)." With Faraday's Laws it became possible to correlate proportionally the tension of the pile with the involved chemical affinities and in this way answer a criticism often raised by the contactists.

The chemical theorists eagerly welcomed this support from Faraday's Laws. For example, in 1836 De la Rive stated that (27):

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.

Friedrich Mohr believed, probably wrongly, that a large majority of Europe's scientists now followed Faraday in support of the chemical theory (28). Yet, although Faraday's Laws were welcome ammunition to the advocates of the chemical theory, they did not seriously change the situation. They certainly did not lead to a defeat of the contact theory or to a conversion of Pfaff and his allies.

With his seminal 1840 paper "On the Source of Power in the Voltaic Pile" Faraday launched a new and forceful attack on the contact theory. Apart from citing a wealth of experimental data (little of which were new), he now considered the question in the light of general principles of natural philosophy. Faraday argued that the contact theory was "improbable" because it violated what would soon be known as the conservation of force, an early version of the concept of energy conservation (29):

... 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 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 forever.

Faraday repeated his view 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 (30)." He undoubtedly referred to Pfaff, among others, who was unconvinced by Faraday's arguments and continued his life-long fight against the chemical theory. At the third meeting of Scandinavian Scientists in Stockholm in 1842, a young Danish scientist, Christian M. Poulsen, delivered a polemical anti-Faraday address that was based to a large extent on Pfaff's most recent experiments and arguments (31).

As late as 1845 the 72-year-old German scientist defended Volta's contact theory against the chemical challenge. His strategy was largely the same as in the controversy with De la Rive, namely to criticize Faraday's experiments and conclusions by his own counter-experiments. Pfaff suspected Faraday to be biased and his experimental results to be influenced by his wish to prove the chemical theory (32):

As a staunch defender of Volta's contact theory of the galvanic chain, I found myself doubly challenged ... to check with the utmost impartiality Faraday's reasons. ... I soon realized that Faraday, in his polemics against Volta's views, had not done the matter full justice, and that he maintained the chemical theory with a kind of passion and endeavored to secure its triumph; for this reason I became suspicious [and doubted] if all of the new experiments reported by Faraday were correct.

But Pfaff also addressed Faraday's more philosophical objections against the contact theory. He argued that the contact force, contrary to chemical forces, was a primitive power that was neither in need of explanation nor restricted by either Faraday's principle of inexhaustibility or Mayer's new principle of force conservation. According to Pfaff, the contact force belonged to the same category as gravity, "which indestructibly and inexhaustibly maintains the life of the large masses on whose motions the order of the universe depends, without its needing any nourishment from the outside that repeatedly rekindles its activity (33)."

Pfaff's 1845 book was primarily directed against Faraday, and secondarily against Schönbein and Gmelin; but it is also of interest because it included the first discussion ever of J. Robert Mayer's 1842 paper on the mechanical equivalent of heat (34). Mayer's publication, in which he introduced the idea of conservation of energy (or force), was later to be recognized as a landmark paper in the history of science; but initially it was ignored by almost all scientists. The exception was Pfaff,

who gave a detailed and critical account of Mayer's view (35). Mayer acknowledged the discussion of the "very distinguished scientist" and in his autobiographical notes he referred gratefully to Pfaff.

One may think that Pfaff was just a stubborn and possibly senile defender of orthodox voltaism, who failed to realize that with the principle of energy conservation "the contact theory had been dealt a mortal blow (36)." But this was not the case. The acceptance of the law of energy conservation did not imply that the chemical theory became universally accepted and the contact theory discarded. Although the chemical theory became much more popular in the 1840s, it was inadequate to replace completely the contact theory. At the time of Pfaff's death the controversy was in decline, and most scientists had lost interest in what previously had been a hotly debated question. The reason was not that the question had been resolved, however, and for several more decades the chemical theory and the contact theory continued to coexist.

At last by 1850 it had become clear that the Volta problem could not be satisfactorily solved within the limits of contemporary science and that a phenomenological approach was to be preferred. Such an approach invited compromises between the two camps. It was only in the 1880s, following progress in electrochemical theory, that the situation changed and it became possible to understand the pile in chemical terms, at least partially. "The chemical theory has fought its way back," Ostwald asserted in 1896, adding that it had won "final victory (37)." Ostwald's optimism was premature, however. The problem of the origin of the voltaic force was even more complicated than he imagined. It was only solved about 1940, when it turned out that both of the rival views, the chemical theory and the contact theory, were needed in order to account fully for voltaic effects (38). It was a conclusion that Pfaff would not have liked.

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- 38. For aspects of the later phase of the controversy, see Kragh, Ref. 18; A. W. Porter, "The Volta Effect," Rep. Brit. Assoc. Adv. Sci., 1928, 21-34; and S. Ross, "The Story of Volta Potential," in G. Dupbernell and J. H. Westbrook, Ed., Selected Topics in the History of Electrochemistry, The Electrochemical Society, Princeton, NJ, 1978, 257-270.

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