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Theodor Grotthuss: brilliance against all odds

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Theodor Grotthuss (1785–1822) was a Lithuanian chemist and physicist who made hugely important and lasting contributions to the fields of fundamental electrochemistry, photochemistry and thermodynamics in his lifetime. He produced visionary work despite being persistently disadvantaged compared to his contemporaries. This article will discuss key moments in Grotthuss' personal and scientific story, starting with an introduction setting the scene of early 19th century electrochemistry with the invention of the Voltaic Pile by Alessandro Volta.

Keywords: Theodor Grotthuss, Grotthuss mechanism, Alessandro Volta, electrolysis, Humphry Davy

INTRODUCTION: VOLTA'S PILE

On 20 March 1800, Alessandro Volta, esteemed Professor of Experimental Physics at the University of Pavia, Lombardy, sent a letter to the editor of the Royal Society's principal publication *Philosophical Transaction of the Royal Society* detailing a new remarkable invention: the Voltaic Pile (Fig. 1) [1].

Volta (Fig. 2) was influenced by the earlier work of pioneer Luigi Galvani, who noted the effects of electrical energy in his now classic experiments with the dissected legs of frogs. Volta's own genius, though, was to realise that electrical energy may originate instead from the contact of different metals, rather than Galvani's assertion that the energy originated from organic means within the muscles and fibres of the legs themselves. Volta's 'contact theory' was much closer to the now realised chemical origin of galvanism. To prove this, Volta constructed an apparatus consisting of a series of copper and zinc disks, connected by wetted card, in a vertical fashion, hence the name 'pile'. Volta found that the pile could produce

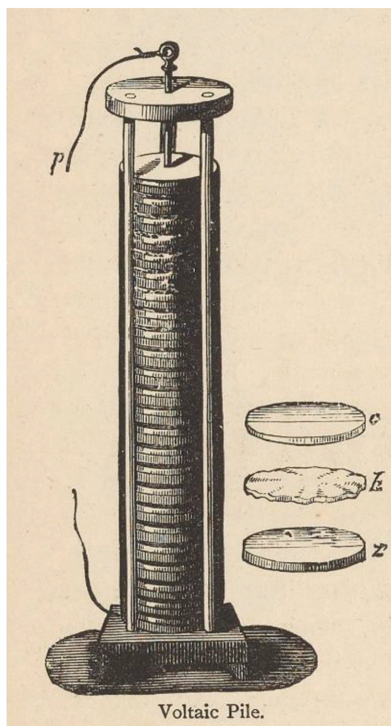

Fig. 1. Illustration of the Voltaic Pile, reproduced from Ward, Lock & Co., Wonders of Electricity and the Elements, London, 1870. Public Domain

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a persistent source of electrical energy in a manner previously unattainable [2].

In an act of what today would surely be considered serious editorial malpractice, the editor, Sir Joseph Banks, immediately shared Volta's letter before its first reading at the Royal Society in London with several of his colleagues [2, 3]. Amongst the group of scientists to learn of the pile before its public announcement were Anthony Carlisle and William Nicholson. Notably, Nicholson was editor himself of a popular journal in England at the time, the *Journal of Natural Philosophy, Chemistry and the Arts*, through which he would publish much of his own work [3].

Upon learning of the pile, Carlisle and Nicholson rushed to construct and experiment with a version of their own. After recreating the observations of Volta, the pair began to experiment with passing the currents generated by the pile into aqueous solutions, discovering the then perplexing effect of the electrolysis of water. Nicholson published the results of their experiments in the July edition of his own journal [4]. Nicholson and Carlisle at least afforded Volta the 'honour' of being named in their work; also appearing in this edition were experiments, detailing use of the pile, by William Cruikshank, who did not mention Volta by name anywhere in his publication at all [5]. Volta's Letter was finally published in *Philosophical Transactions* in late 1800, months after Nicholson and Carlisle's experiments had appeared in the literature [1].

Fig. 2. Sketch of Alessandro Volta. Reproduced from *Routledge's Popular History of Science*, London, 1881 (Reference 2). Public Domain

An often-overlooked part of Volta's story, highlighted by Luigi Fabbrizzi in his essay on the subject [3], is that in the months leading to his invention of the pile the University of Pavia, of which he was professor, had closed between April 1799 and June 1800. The region in which the University was situated changed hands between French and the Austro-Russians in the years leading up to 1799. Returning to Lombardy, the Austro-Russian coalition forcibly closed the university and fired its academics and staff, including Volta, presumably for demonstrating their allegiance to French occupation in the years prior. Without a laboratory, students, or funding, Volta worked from a makeshift home laboratory in his estate in Como. It was from here he would construct the first pile [3].

Despite the difficult circumstances of its conception, Volta's invention had generated considerable excitement in the scientific community in London, and the premature experimentation by those which had learned of the pile before its public announcement had raised new questions. The mechanism of action of the pile in the electrolysis of water first documented by Nicholson and Carlisle in their early experiments took centre stage of this debate in the years following [6].

GROTTHUSS

Theodor Grotthuss was born in Liepzig, 20 January 1785, to Elizabeth Eleanore von Grotthuss and Dietrich Ewald von Grotthuss. The family were on an extended trip to Germany at the time of Theodor's birth. The modern branch of the von Grotthuss household, having originated in Westphalia in the 12th century, resided in Courland (now northern Lithuania) within a family estate in the village of Geddutz (now Gedučiai), south-east of the town of Žeimelis (see Fig. 3). The family was undoubtedly influential in the region; Grotthuss' godfather, Christian Felix Weise, would successfully secure Theodor a studentship at the University of Leipzig only a few months after he was born [6, 7].

Fig. 3. Modern map of Lietuva (Lithuania) showing the location of Gedučiai, the estate where Grotthuss lived and worked. Map (border) data from OpenStreetMap (openstreetmap.org/copyright)

Theodor's father Dietrich suffered from a serious illness, most likely pancreatic in origin, which would worsen soon after Grotthuss was born. Prompted by this, the family moved back to their estate in Gedučiai mid-1786. Dietrich would succumb to his illness in September that same year. Grotthuss grew up on the estate, receiving a highly traditional education in arts, literature, classics and music, and developing a skill for the pianoforte, which he had inherited from his father. Along with a friend, Heinrich Bidder, a pharmacist's apprentice in nearby Mitau (now Jelgava, Latvia), Grotthuss would conduct scientific experiments in secret, away from the gaze of his tutors [7].

At the age of 18, Grotthuss moved to Leipzig to study at the University, where he was already a student thanks to the efforts of his godfather 18 years earlier. Discouraged by the more traditional attitudes towards natural philosophy held by many of his teachers, he transferred to the École Polytechnique, Paris, in late 1803. There he studied under contemporaries such as Fourcroy, Haüy, Bertollet and, notably, Gay-Lussac, who had recently demonstrated that water was comprised 2:1 hydrogen to oxygen [6, 8].

It becomes clear in recounts of Grotthuss' life that an illness began to ail him sometime in 1804, at the age of 19. Grotthuss seemingly inherited the disease that had killed his father shortly after he was born, and this disease would continue to affect him for the rest of his life. Pressured also by the impending war between Napoleonic France and Tsarist Russia, Grotthuss moved to Italy in September 1804. Now in Naples, Grotthuss actively participated in expeditions up Mount Vesuvius with his counterparts [6].

At some point in 1805, Grotthuss makes the acquaintance of Dr. William Thomson, a British physician, minerologist and anatomist [9].* Thomson was a physician at the Radcliffe Infirmary, Oxford, and lecturer at Christ Church, University of Oxford, having previously studied mineralogy at the University of Edinburgh [9, 10]. In the autumn of 1790, Thomson suddenly renounced his numerous titles and fled to Italy, on account of a scandal relating to his homosexuality, then a capital crime [9]. Thomson would gift Grotthuss a version of Volta's pile, with which he would begin conducting experiments with immediately [6, 7].

Readers familiar with the story of Grotthuss will almost certainly be aware of his landmark pamphlet published in 1806, '*Mémoire sur la décomposition de l'eau et des corps, qu'elle tient en dissolution à l'aide de l'électricité galvanique*' (Memoir on the decomposition of water and of the bodies that it holds in solution by means of galvanic electricity). This seminal work [11], reproduced and described in detail elsewhere [6, 7, 12–14], described the mechanism for the decomposition of water documented by Carlisle and Nicholson six years prior. Grotthuss used an atomistic approach to describe the movement of 'corps' through solution between electrodes, laying conceptual foundation for the now well-understood 'Grotthuss mechanism' (Fig. 4).

It is important to evaluate Grotthuss' work in the context of scientific understanding at the time. Until this point, many attempts to explain the so-called 'Nicholson Paradox' of the splitting of water assumed 'electricity' to be a fluid component separate to water entirely [15], or propose hypotheses which adhered to strictly traditional views which denied atomism altogether [16]. Grotthuss' genius was to unite atomistic and 'natural force' philosophies together – using atomism to describe the mechanism of the movement of distinct 'corps' between electrodes, while admitting that the 'corps' themselves must have an element of polarisability.

* Thomson is identified here for the first time in the Grotthuss literature, to the best of the authors' knowledge. According to R. T. Gunther (1936), Gay-Lussac, Humboldt and others had visited Thomson in 1805, around the time Grotthuss received the pile. We entertain the possibility here that Grotthuss may have been with them for this visit, although details are scarce.

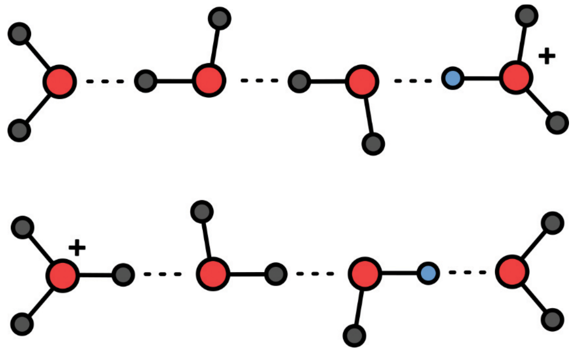

Fig. 4. Illustration of the Grotthuss mechanism. The apparent transmission of a proton across a series of water molecules (red oxygen, grey hydrogen) in a hydrogen-bonded network is a series of reconfigurations in a chain

While accepted without much criticism by the scientific community, the long-term impact of Grotthuss' 1806 paper was limited. It was principally due to the actions of Ostwald in the early 20th century that cemented Grotthuss' place in the history of physical chemistry; Ostwald would publish a special edition of '*Klassiker der exakten Wissenschaften*' dedicated to Grotthuss, bringing his work back into the mainstream scientific consciousness [17]. The 'Grotthuss mechanism' itself was immortalised by Danneel in 1905 who used it to explain the abnormally high mobility of protons in water, as it is taught to chemistry undergraduates today [18].

After publishing his seminal paper, Grotthuss travelled back to Paris via Milan and Turin. He remained in Paris for another year, working in the laboratories of Vauquelin, where he publishes work on topics of dendrites [19] and organic chemistry [20]. At some point after his 1806 paper was published, Grotthuss decided to formally change his name from his full traditional title of 'Christian Johann Dietrich' to Theodor, possibly as an attempt to distance himself from his aristocratic ancestry in what was now a staunchly republican nation [7].

Presumably ailed further by his condition, Grotthuss returned to his home estate in Gedučiai in the autumn of 1807, where he would remain for the rest of life (bar a 6-month visit to St. Petersburg in 1812 which stimulated his work on photochemistry). The move away from France would not spell the end for Grotthuss' scientific exploits, however. He would continue to work from a home-built laboratory (much like Volta years prior) on his mother's estate, and would continue to publish works on various aspects of photochemistry [21] and the combustion of gases [22, 23], albeit now from a much less well-equipped laboratory and in a much less well-connected location.

Grotthuss' work on the topic of photochemistry was equally as profound as his electrochemistry. He noted in 1815 that light emitted from a sample of the mineral *chlorophane* was not the 'same' as absorbed [21], providing one of the earliest accounts of the phenomenon now known as phosphorescence. Attempting to build a mechanistic framework for these observations, he theorised that light split into charged components at the surface, which he denoted 'E+' and 'E-', and the interaction of those charged components with the structure of the mineral led to the emission of different colours of light [21]. Later, he would conclude that all metals must contain some 'E-' component, decades before the discovery of the electron in 1895 [24]. Studying solutions of iron thiocyanate in 1817, he observed that chemical change exclusively occurs upon absorption of light (Fig. 5). This 'law' would be independently confirmed by John W. Draper in 1842, leading to the eventual establishment of the Grotthuss–Draper Law of Photochemistry [24].

Grotthuss' acquaintance with Gay–Lussac, who produced some of the first work on gases in the early 19th century, would inspire Grotthuss to conduct experiments of his own on flammability. From these experiments he made significant contributions; he was the first to document the importance of pressure on the combustibility of gaseous mixtures in 1809 [25, 26]. Further to this, Grotthuss would note, in a paper published in Schweigger's *Journal für Chemie und Physik* in 1811, that flame was unable to propagate through small apertures and tubes [22]. Grotthuss explained this effect as due to increasing 'rarefaction'

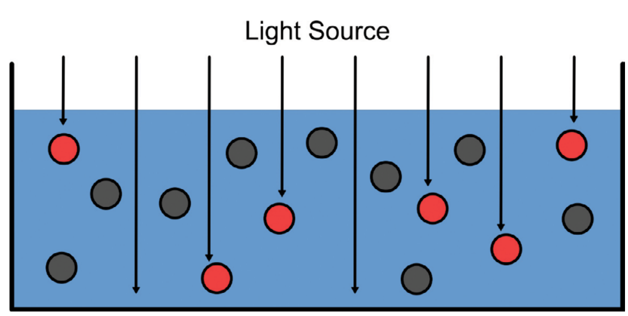

Fig. 5. Illustration of the Grotthuss–Draper Law of Photochemistry. Only light absorbed by a system may enact chemical change

within the small apertures significantly reducing their flammability.

This observation mentioned became the subject of an extended disagreement between Grotthuss and one Humphry Davy, eminent British scientist and aristocrat. It is on this topic we will focus the next section of this article.

DAVY AND THE MINER'S LAMP

Coal mining in the early 19th century, accelerated by the development and use of steam engines, was increasingly dangerous; activity in deeper mines revealed a particular danger: 'firedamp'. Flammable gas build-up in deep coal pits, ignited by the candles workers used for light, lead to hundreds of deaths in the years prior to 1815. The problem of lighting in the mines became the focus of many contemporary scientists.

Humphry Davy (Fig. 6) presented his contribution to this problem in a demonstration at a colliery in Newcastle, November 1815. Inspired by earlier crude designs by William Clanny (whom he affords to mention in communications), it consisted of a simple paraffin lamp, the flame of which was surrounded by a wire gauze. This gauze, as Davy demonstrated, would not allow the passage of gases ignited by flame through, preventing the explosion of 'firedamp' in its immediate surroundings. In his initial communication to his fellows at the Royal Society on 9 November 1815, Davy in fact describes two lamps: one which uses a gauze to prevent passage of flame as described above, and another which uses small tubes to admit air to a glass lamp from the base [27]. Importantly, Davy does not mention Grotthuss anywhere in this communication, leading to the impression he discovered the effect of the impassibility of flame on his own.

Fig. 6. Portrait of Humphry Davy by Thomas Phillips (1821), from the collections of the National Portrait Gallery, UK. Public Domain

Janis Stradiņš, who contributed much to the literature on the topic of Grotthuss and the story of the miner's lamp, notes it is unlikely that Davy had not encountered the publications prior to his work [25]. Grotthuss' paper describing the effect was translated to English and published in Nicholson's Journal in 1813, meaning they were entirely accessible to Davy at the time of his 'invention' [28].

Adding to this, Davy and his associates had a history of making the most of their influence and prominence when it came to public disagreements. George Stevenson, foreman at a colliery in Killingworth, Newcastle, had also independently designed a lamp similar in function to Davy's and demonstrated its efficacy a few weeks prior to the reading of Davy's letter to the Royal Society. Stevenson was no stranger to the danger fire-damp posed to his workers; he had gone down into the pits himself a year before to help put out a fire caused by the use of candles as light sources [29]. Once the similarity between the designs was pointed out by Stevenson and his associates, Davy and his colleagues at the Royal Society opted to publicly smear Stevenson as a liar and cheat; Alexander Tilloch, then editor of the *Philosophical Transactions of the Royal Society*, asserted that Stevenson *must* have stolen the idea somehow [30]. A parliamentary committee later attributed equal credit to the invention between Davy, Stevenson and Clanny, who had inspired Davy's initial designs, putting to rest the claim that Stevenson had 'stolen' the idea [31].

A similar tactic was engaged by Davy when approached about Grotthuss' ideas. Only after a visit by Johann Schweigger, then editor of the German *Journal für Chemie und Physik*, in 1816, would Davy mention Grotthuss in the matters of the impassibility of flame. In a paper published in 1817, despite his description of Grotthuss as 'ingenious', Davy criticised his attempt to explain the phenomena, finding that Grotthuss' theory of 'rarefaction' at odds with his own experiments. He claimed to show that reduced heat propagation was the only factor in gas in-flammability [32].

Grotthuss, along with a few of his compatriots, were evidently frustrated by this. Grotthuss responded in 1818, describing his difficulties with communication and his lack of proper equipment in his home-built laboratory [33]. He even showed that he had already performed and documented some of the experiments Davy reported, proving he had not considered his research thoroughly enough. He wrote: '*I regret that Mr. Davy does not once cite the specific text or page number where my experiments can be consulted, either in the original text or the translation*'. Further, in a footnote, he writes: '*Of course, had he done so, one would have found upon looking that several of the phenomena he presented as entirely new discoveries had long since been observed and described*' [33].

Davy, himself struggling with poor health by this time, never responded to Grotthuss, citing a lack of available translators [25]. Despite his efforts, Grotthuss does not feature in any modern publications about the miner's lamp, and history has appeared determined to attribute the development of the lamp entirely to Humphry Davy.

PERSPECTIVE

Introducing this article with the story of Alessandro Volta was intended to serve two purposes: the first, to introduce the scientific problem that Grotthuss would solve so completely in his now classic paper in 1806, placing him amongst other great names in the story of the birth of electrochemistry in the early 19th century. The second was to highlight the parallels between the story of Volta and that of Grotthuss.

We hope it is clear now that both Europeans were both significantly disadvantaged compared to their contemporaries at the Royal Society. Volta was displaced from his institution due to political turmoil in the year leading up his introduction of the 'pile', having to work in a makeshift laboratory with little of the equipment, resources or assistants a distinguished professor of the time would otherwise have access to. Grotthuss also produced

Fig. 7. 'Portrait of Theodor Von Grotthuss' by Meisenbach Riffarth & Company. Pub. Engelmann, Th. W. (Th. Wilhelm), Leipzig. Date unknown. Courtesy of Science History Institute, Philadelphia, USA. Public Domain

much of his work in the last 15 years of his life from a similar situation, in a home-built laboratory at his mother's rural estate, with little equipment or communication with the scientific world around him.

Further to this, both authors had their work seriously misappropriated by those in Britain, with both falling victim to cases of blatant plagiarism by the upper echelons of the Royal Society within their lifetimes. A common theme is found within these two stories; those outside of London were treated with a contempt that kept the names of many brilliant minds out of the history books. Grotthuss was perhaps worse off in this regard – Volta at least became a household name, lending his namesake to the fundamental unit of potential.

Grotthuss' work, alone at his home estate, demonstrated quality and curiosity above many in much more fortunate circumstances. This conclusion is reached even without considering Grotthuss' own personal situation. It becomes clear learning about the scientist's life that hereditary ill health played a prominent role in many of the decisions he would make, such as to leave France in 1807 to return home, eventually culminating in his choice to take his own life in March 1822 at the age of 37 [6, 7, 14].

Despite those hardships, Grotthuss produced incredibly important and lasting contributions to electrochemical, photochemical and thermodynamic understanding at the time, even rivalling that of those who were equipped with the very best facilities. It is for this reason that Grotthuss should be considered a true genius.

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