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In the Wake of Volta's Challenge: The Electrolysis Theory of Theodor Grotthuss, 1805

Alessandro Volta's invention of the electric battery (1799) became a major challenge to his contemporaries. This challenge can be best expressed in the form of a query: who shall be the first to explain the mysterious action of the voltaic pile? This challenge attracted the best men of science of the age, especially those already working in the field of electricity and chemistry, who tried to explain the nature and mechanism of the production of electric currents.

One such person was Theodor Grotthuss (1785-1822), who although born in Leipzig, Germany, was of German Baltic stock and spent most of his short life on his mother's estate in Lithuania. He became acquainted with Volta's pile while on a long visit to Paris (l803-5) and did most of his research while in Naples and Rome (l805-6).

In the interpretation of the electrolysis phenomenon, Theodor Grotthuss gave Volta's pile a particular importance. For him it was not just a generator of up till now not well understood galvanic phenomena but was also a model of a real "electropolar" system that existed in Nature and that manifested itself through this newly created artifact of Volta's invention.[1]

According to the explanation provided by Grotthuss, and today known as his first theory of electrolysis, Nature's foundation is based on electrical type polar opposites, what he called the elementary molecules.[2] During electrolysis, water molecules will orient themselves into polar chains linking the electrodes into a unified system. The polarized molecules become the continuation of the copper-zinc couples that make up the pile. In his memoir published in Rome in 1805, the-twenty-year old Grotthuss said:

[1] See GROTTHUSS (1805).

[2] At that time there was no clear definition of the concept of molecule. Matter particles were differently defined. Thus, Grotthuss was learning towards calling them just that "particles". From a study of his writings, it is clear that he uses the term "molecule" when referring to matter parts in a solution, whereas he uses the word "particle" for matter fragments that are not dissolved. The overall impression gained from the study of his texts is that Grotthuss's "molecule" is closer to "ion", and that he was pioneering this concept.

> Au moment qu'on établit une courant d'électricité galvanique dans cette eau, la pôlarité électrique se manifeste entre ses molécules élémentaires, de façon que celles-ci sembleront constituer le complément pile en action.[3]

The above is based on an experimental observation that crystal growth occurs always along the direction of the flow of current.[4] Thus, in the interpretation provided by Grotthuss, the source of the electrical current is to be found in the copper-zinc stack of elements that make up the Volta pile and the aligned molecules in the solution between the electrodes, the two together constituting a united operating system.[5]

It is worthwhile to emphasizing that by incorporating Volta's pile into this universal Nature's polarization system, Grotthuss creates the concept of influence between electrodes occurring along parallel lines. Some forty years later Michael Faraday developed his lines-of-force model from this concept. Faraday several times acknowledged in his papers[6] that the starting point of his work was Grotthuss' 1805 electrolytic theory.[7] This theory, the starting point of his reasoning and the concept of material lines, was a necessary but not sufficient condition for Faraday's development of the concept of electric field.

Before we examine the explanation for the decomposition of water that is provided by the 1805 electrolysis theory produced by Grotthuss, let us review the circumstances under which Volta's invention challenged scientists to provide explanations of its operation. This is necessary because no invention and no idea appears in a vacuum. Everything has antecedents and premises.

Shortly after Volta's invention it became clear that a continuous electric current creates chemical changes. Anthony Carlisle discovered that metals are deposited on the electrodes from a solution of metallic salt, while his friend J.W. Nicholson discovered that water decomposed during electrolysis, and that hydrogen was generated at one electrode and oxygen at the other. This last effect compelled scientists to look for an explanation as to why water components appear in different parts of the vessel.

We have to keep in mind that the first reactions to these various voltaic phenomena came from within the existing paradigm of static electricity. In the last decades of the eighteenth century and the first two decades of the nineteenth, only electrostatic instruments were used to study any new electric phenomena and the voltaic pile itself. And, obviously, the first explanations were based on the theoretical models and concepts of static electricity. We have to keep in mind that at

[3] GROTTHUSS (1805), pp. 15-6.

[4] *Ibid.*, p. 5.

[5] The artifact built by Volta had different names – battery, pile, column.

[6] FARADAY (1839), p. 137.

[7] In his published work, the name of Grotthuss appears frequently, and therefore it would be impossible to cite all references to his name.

this time French scientists had made the greatest strides in studying electrostatic phenomena and they naturally were the first to provide explanations for the new electric phenomena.[8]

Jean Baptiste Biot was the first in order to explain the generation of a constant electric current in a voltaic pile, he started by asserting that the pile was generating a "fluid" that was electrostatic in nature which was the effect of two different metals in contact. Furthermore, he thought that the electromotive force that appears in the battery between the metallic plates is not involved in the flow of this electric "fluid" because the contact force of electrostatic origin, separating the different fluids, prevents their mutual interaction. In addition, the conductive pasteboard inserted between the plates allows fluids to stream in different directions. The inserted pasteboards interfere with the direct interaction of opposite fluids. A chain of impulsive stimuli becomes perpetually impelled stream, a torrent that is composed of a tremendously large avalanche of short and imperceptible discharges.[9]

Visualizing this way Volta's battery was not arbitrary because Biot based his reasoning on research and empirical observations made by a series of investigators that clearly linked galvanic phenomena with chemical processes.[10] But Biot's explanation neither went beyond the classic static model developed for electrostatics, nor could he explain why and how this final polarization takes place. In any case, he seriously doubted whether the experimenters provided sufficient accuracy in their work. In his contribution he tried to show that chemical phenomena can be explained in terms of electrostatics.

In his well-known *Traité de physique* (1803) René-Just Haüy stated that observed "facts" in Volta's battery are of purely electrostatic origin. Therefore, according to Haüy, contact-induced electric power cannot be the only culprit of the variety of impulses. For him, the constant current produced by Volta's pile is due to a process of successive, fast and discrete impulses ("attaque par une succession rapide de petites impulsions").[11]

If Biot is cautious in his portrayal of electric current as a series of short and imperceptible impulses, then Haüy clearly asserts this idea, expanding it to emphasize the concept of successive, cascading and spasmodically developing series. It was into this polemical clash of views that Grotthuss stepped in when he arrived in Paris from the distant shores of the Baltic Sea.

An analysis of the scientific legacy of Grotthuss provides sufficient grounds to claim that he transferred to the province of physical and chemical phenomena what Biot and Haüy were developing along the lines of an electrostatically defined

[8] See BROWN (1969), pp. 68-9.
[9] See BIOT (1803), pp. 5-45.
[10] This list includes F. Cuvier, W. Nicholson, J. Ritter, H. Davy, W. Wollaston, and others.
[11] HAÜY (1803), p. 56.

model.[12] He did this courageously, even though he did not yet have time to review all that had been published on the subject. His merit resides in his creative ability to recast known facts into a new mould.

In the theory proposed by Grotthuss, the process of decomposition of water and the transfer of "action" occurs along the lines or chains that are formed by molecules. Since these molecules are carriers of both kinds of electricity, they polarize correspondingly between the opposite electrodes of the battery. Where the molecular chain touches the electrodes, the water molecules split, separating themselves into water molecule's parts. At the negative electrode hydrogen appears, while oxygen collects at the positive electrode. This molecular splitting and recombination takes place in all molecular chains, stretched between the electrodes.[13] The water molecules exchange their component parts instantly, mutually and alternatively,[14] giving rise to a transfer by relays so that an advance takes place in opposite directions along all aligned molecular lines. The overall effect of this process is visible in the vessel where the electrolysis takes place: hydrogen and oxygen separate in the solution that is in contact with the opposite electrodes.

The electrolytic theory of Grotthuss in providing a model for the decomposition of water not only explained the then mysterious "Nicholson effect", but, most important, raised the idea of leaping interactions, which was applied by him to the concrete case of the transfer process that occurs in the vessel where electrolysis takes place. Within this idea lies concealed the principle of least common multiple, for the first time raising the most basic quality of atomism, namely, the discreteness of material objects, their divisibility – from the structure of matter to the sphere of phenomena, that is from statics to dynamics. Within his theory also lies concealed as a hint still not clearly expressed – that these acts of leaping interaction that instantaneously permit molecules to exchange their component fragments are determined by their quantity. In other words, here we have to keep in mind that these interactions are determined by their magnitude. This in turn means that the transfer of electric "fluid" and of matter in the microscopic world occurs in discrete and finite portions, whose size is the magnitude of the component parts. The history of physics bears witness that only after a century did these quantitative interactions became finally perceived as a fundamental principle.

The scientific community received this electrolytic theory of Grotthuss without any particular argument. It was a theory that explained well the electrolysis of water and that gave the voltaic pile the status of Nature's fundamental phenomenon. In this theory, Grotthuss considers the molecule as a union of electrical opposites. The main components of molecules carrying these opposite electric "states" or fluids make – thanks to these states – the stable molecule. In this resides our belief that Grotthuss

[12] STRADINŠ (1966); KRIKŠTOPAITIS (1976), pp. 251-6.
[13] See GROTTHUSS (1805), p. 16.
[14] See *ibid.*, p. 17.

was one of the first to express this idea, namely, that a molecule is a material unit, a carrier of opposite charges embodying a physical and chemical unity. Based on this idea of electropolarity of molecules somewhat later H. Davy developed his concept of chemical affinity and J.J. Berzelius that of chemical dualism, which was influential in the further development of chemistry.

More than a decade later, Grotthuss widened the potential of his idea.[15] He claimed that even when there is no electrical influence, in a solution there still takes place this constant interchange of their component parts among all the molecules. Without any outside influence these closed molecular chains and rings form these jumping acts of electrical exchange of the molecule component parts. But this spontaneous galvanic phenomenon is not noticeable because there is a balance between the electric forces present among the molecules. When an outside electricity source is imposed, this equilibrium and spontaneous exchange breaks down. Now the molecular chains stretch out between the electrodes and the electrochemical effects begin to appear, including the decomposition of water.

It is not difficult to understand that the ideas developed by Grotthuss lead towards the next step – the formulation of a concept of ions – the fragments of molecules that exist in solutions. About fifteen years later Faraday determined the laws of electrolysis.

We now turn to the question of what circumstances and factors were decisive in Grotthuss's ability to suggest explanations that adumbrated important features of the electrolysis process and pointed to important concepts for the future of science. An analysis of his scientific work suggests three factors.

First, his deep conviction that atomism reflects the structure of the material world. This was in line with the revival of atomism that is linked with the contributions of John Dalton.

Second, recognition that F.W.J. Schelling's idea about the "conflict" of forces really discloses the nature of the chemical and physical phenomena (except for his claim that electricity is non-material). In his electrolysis theory Grotthuss binds the statics of structures with the interactions and the dynamics of the process. His suggested explanation for the transfer of electricity and matter had in its framework a fruitful perspective, in that this process of polarization was paving the way for Humphry Davy's chemical affinity theory and Jons Jacob Berzelius's electrochemical dualism system. It is interesting to point out that Grotthuss valued in his theory not the concept of leaping transfers of the components of the polarized molecules but the idea of molecule electropolarization. The latter was to form the basis of the further evolution of our knowledge of the processes that occur in the microscopic world.[16]

Third, and last, a crucial factor in Grotthuss's development as a scientist was the fact that his thinking was not shaped by the electrostatic stereotypes or by deference to authority.

[15] See GROTTHUSS (1819), (1819a), (1820).
[16] STRADINŠ (1966), p. 61.

We mentioned previously that when Grotthuss began developing his views on electrolysis, he had not thoroughly reviewed all the literature that others had published on this topic. That made him less bound to the scientific dogmas of others. Grotthuss created his theory starting from scratch and basing himself on what he found out himself while he resided in Paris (1803-5). In Paris he attended the lectures of C.L. Berthollet, A.F. Fourcroy, L.N. Vauquelin, L.J. Thenard, R.J. Haüy, and others. He particularly liked the first two, while Vauquelin and J.L. Gay-Lussac acquainted Grotthuss with experimental habits and laboratory practices. In 1805, he left Paris for Ita1y, where he participated with Gay-Lussac in Alexander Humboldt's expedition to Mount Vesuvius to do research on the eruption that took place earlier that year. It was also in Italy that Grotthuss carried out the basic research in electrolysis, and thinking over the results, sat down to write in September of l805 his celebrated Memoire in which he set forth his theory. Three months later it was printed in Rome as a *pamphlet*.

The memoire was well received both in Italy and in several other countries by the scientific community.[17] In 1806 it was translated into English and German, and reviewed in the main scientific journals.[18] When Grotthuss returned to Paris by year's end[19] after a brief tour of Florence, Milan and Turin, he was accorded an excellent welcome as the author of the well-known theory of electrolysis and elected an honorary member of the Société Galvanique. While in Paris, he spent some additional time working in the laboratory of Vauquelin. In 1807 he finally returned to his mother's estate in Geduciai, Lithuania. He established his own laboratory, which although primitive allowed him to conduct meaningful scientific research until 1822 when, overcome by depression and the pain of his inherited disease, he committed suicide.

Theodor von Grotthuss (1785-1822) belonged to an old and distinguished family of Courland nobility, which came to the Baltic region from Westphalia at the end of the fifteenth century. The aristocracy of Courland, composed of German emigrants, created a German culture which valued education highly, and was able to express itself independently as the bearer of the new Courland aristocracy's traditions, albeit adjusted to the political, social and ethnic characteristics of the Baltic region. Grotthuss grew up in this tradition, but his way of thinking and the style of his writing bear witness to the fact that in Paris he became a pupil of French science and remained so until his death.

There were other scientists from the Baltic region who responded to the challenge produced by Volta's invention. In l801, G.F. Parrott and his assistant D.J.

[17] See for evidence the newspapers *Efemeridi di Roma*, 12 (1806); Gehlens *Journal für die Physik, Chemie und Mineralogie*, 5 (1806), pp. 110-8, and a number of other periodicals.
[18] See *Annales de chimie et de physique*, 58 (1806), pp. 54-74; Tilloch's *Philosophic Magazine*, 24 (1806), pp. 330-8; *Reportery of Arts*, 9 (1806), pp. 365-70.
[19] In Rome, Grotthuss visited the laboratory of D.L. Morichini, but there is no evidence that he met A. Volta while he was staying in Italy.

Grindel produced in Riga the first experiments in the region using Volta's pile. The following year, and by then at the University of Dorpat, Estonia (today Tartu), Parrott created a theory that explained galvanism as a chemical oxidation.[20] According to Parrot, chemical processes generate electrical energy. Oxidation is not the result but the cause of galvanism. Another scientist, Stefan Stubielewicz traveled extensively during 1802-4. In his study tour, he visited Austria, Germany, and Italy, but he spent most of his time in Paris. He attended lectures at the Ecole Polytechnique. Upon his return, he became professor of physics in l807 at the University of Vilnius.[21]

Summarizing all the above, I would like to draw the reader's attention to the following: first, Volta's discovery was grasped by scientists as an earthshaking challenge and became quickly and widely disseminated. It resonated even in remote centers of European intellectual activity. Second, Volta's battery required scientists to provide explanations of the galvanic electricity generation and forced the rejection of the old electrostatic models. This paved the foundation for electrochemistry and built the road for the development of electrodynamics.

(I would like to thank professor Janis Stradins (Riga) for his intellectual support and for pioneering the research on Theodor von Grotthuss, and to professor Romualdas Sviedrys (New York) for his comments and help with the translation into English).

[20] G.F. Parrot's ideas were presented in various journals, the most important being Gilberts *Annalen der Physik und der physikalischen Chemie*, 12 (1802), pp. 49-73.

[21] The University of Vilnius in the 18th century was known as "The Principal School of the Grand Duchy of Lithuania". Upon the conquest of Lithuania by Russia in 1795, eight years later (1803) its name was changed by imperial edict to "Imperial University of Vilnius".

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