# THEODOR VON GROTTHUSS (1785-1822) – A TRAIL BLAZER

Bruno Jaselskis, Carl E. Moore, and Alfred von Smolinsk, Loyola University of Chicago

Two hundred years ago Theodor Grotthuss published a major paper entitled "*Mémoire sur la décomposition de l'eau et des corps, qu'elle tient en dissolution a' l'aide de l'élecrticite galvanique."*(1) In a short time this document was reprinted in other journals (2, 3) and was translated into English (4). In this paper Grotthuss presented an electrolysis concept based on physical-chemical phenomena rather than on the prevailing established electrostatic interpretation of the galvanic process. He perceived the battery not only as a galvanic generator but also as a polarized system composed of particles (molecules) of opposing electrical nature. This landmark document laid out new directions for the interpretation of galvanic phenomena. It influenced future investigations carried out by Sir Humphry Davy, John J. Berzelius, Michael Faraday, and others.

This paper was published five years after Alexandro Volta's invention of the electric pile, a device that could provide a continuous electric current for a prolonged period of time. Volta reported this discovery in a letter, written in French, to Sir Joseph Banks, the president of the Royal Society of London (1800). This report of the pile "*On Electricity Excited by Mere Contact of Conducting Substances of Different Kinds,"* appeared in the *Philosophical Transactions* (1800) written in the French language. It was followed by an English translation in September of the same year (5). Volta's paper was a gigantic step from the electrostatic mode of creating electricity and brought with it the challenge to explain the mysterious action of the voltaic pile.

This challenge engaged the best minds of science throughout Europe, in particular those working in the field of static electricity, and especially those who were trying to explain the mechanism of the production of static electricity. Out of the ferment of the times came a young novice scientist, Theodor Grotthuss, a student, eager to absorb knowledge and resolute in his desire to form his own opinions and interpretations uncluttered with the dogma of the established thinking.

J. A. Krikštopaitis, in his interesting book written in the Lithuanian language, titled "Pralenkęs Laiką" (Ahead of the Times), describes the life of Theodor Grotthuss and his scientific contributions. He states (6):

> If Alfred Nobel would have instructed to award a prize for works done a century earlier, T. Grotthuss would have been awarded twice-once for his electrolysis theory and the second for his photochemistry postulates.

Grotthuss was fortunate to be born at the right time, with a high rank in society, and to be endowed with a brilliant inquisitive mind.

## Intellectual Environment at the End of the 19th Century

At the time of Grotthuss's birth the works of natural philosophers of the enlightenment period and the intellectual features of the French Revolution promoted a spirit of confidence in the human mind and ushered in the scientific revolution. Especially, ideas by J. W. Goethe, F. W. Schelling, G. W. F. Hegel, and Immanuel Kant encouraged investigation of nature and existing forces. Added to these insights were Lavoisier's brilliant experimental observations that all processes obey a mass conservation law and that something cannot be created from nothing. These insights and observations merged into a radical view of the world that was quite contrary to that from any previous age and required the application of analytical methodology to grasp the nature of the natural world. In the beginning of the 19$^{th}$ century Newtonian mechanics dominated the description of the natural world. Kant and Schelling tried to question "Newton's despotism" in their discourses on natural philosophy. They treated the world as a dynamic summation of differences that continuously underwent changes. Schelling viewed nature as a precise unity and summation of attractive forces. Force could not exist alone without a counterpart, hence matter was continuously undergoing disproportionation, recombination, and neutralization. Thus, young Grotthuss grew up in a period open for inquiry and discovery.

## Grotthuss's Early Childhood

Ewald Dietrich von Grotthuss and his wife Elisabeth Eleonor, the parents of Theodor, belonged to an old and distinguished family of Kurland (Courland) chancellery nobility. In 1784 the family went for an extended trip to Western Europe. While the parents were traveling through Germany, their son was born in Leipzig on January 20, 1785. Soon after his birth he was baptized and given the names Christian Johann Dietrich. As an adult he chose to use Theodor as his first name. His godfather, a well known German writer, Felix Weisse, interceded with Samuel Friedrick Morus, the Rector of Leipzig University, to obtain a student's matriculation certificate entitled "*Inscriptionis Diploma.*" Thus, Grotthuss, just a five-day old baby, became the youngest student with a title "*C. J. D. Grotthuss Lipsiensis.*" In a letter to the child's father the godfather stated (7):

> Here are all opportunities for your young beloved son, to acquire a great education, a better education than that of his father and ending this letter I say "Amen.

The Grotthuss family decided to stay in Leipzig for a while. Young Theodor's father was an amateur composer and collector of natural science materials. Unfortunately, the father's health was fragile, and while in Leipzig, it took a turn for the worse. In 1785 the family returned to their estate, and few months later his father, Ewald Dietrich von Grotthuss, died from a stomach ailment.

Theodor Grotthuss grew up on his mother's estate in Gedučiai (Geddutz), which on today's map is located in the northern part of Lithuania at the border with Latvia. He was a lonely child who had relatively limited contact with the children in the village. He had to use his mind and imagination to fill in the time. Tutors instructed and trained him at home, as was customary, in the skills of languages, mathematics, art, and literature. Thus, he obtained a sound basic education enabling him to pursue higher education at various universities. At this time it was not necessary for him to get a diploma. The position within the nobility rank determined the success in a career, not a diploma from a university.

## Grotthuss as a Young Scholar

At the age of 18, in May of 1803, the young Theodor Grotthuss left his home for studies abroad, enrolling at the University of Leipzig. However, after attending some lectures there, he became disillusioned because of the lack of new ideas and the shortage of laboratory facilities suitable for experimentation. While in Leipzig some works by Schelling influenced his inquisitive mind. In the fall of the same year Grotthuss went to Paris, where he started studies at *L'Ecole Polytechnique*. He attended lectures of famous professors: C. L. Berthollet, A. F. Fourcroy, Rene-Just Haüy, L. N.Vauquelin, L. J. Thenard, and others. These lectures and laboratory experience had a great influence on his future scientific work. Fourcroy conveyed important ideas on electrolysis, Berthollet on equilibrium, Haüy on crystallization and motion of particles; Vauquelin and Thenard helped to develop his laboratory skills. At the same time the discovery of Volta's battery in 1800 stimulated intensive research efforts at universities and fascinated the minds of scholars including Grotthuss, even as a new student. These discoveries and contacts became an important driving force in his future career.

Grotthuss was influenced by the French revolutionary ideas of rationalism and the democratic way of life. Although of the Kurland nobility, in his public life and in his publications he chose not to use the title **von** and dropped it when he was in Rome in 1806.

Grotthuss's studies in Paris were interrupted when Napoleon declared himself emperor and started preparations for war with Prussia and Russia. Troubled by a recurring stomach-related illness inherited from his father, Grotthuss set sail from Marseilles to Italy with the hope of improving his health. This move provided him much needed rest from his intensive studies in Paris.

In Italy he went to Rome and then to Naples, where he joined a group of scientists, J. L. Gay Lussac, A. Humboldt, and L. Buch, who were investigating volcanism of mount Vesuvius. Under Gay Lussac's guidance he analyzed volcanic gases. While with this group, a British doctor, Thomson [name not available] gave him a Volta's battery pile. This gift was to play an important role in electrical science in that it enabled Grotthuss to study electrolysis, in particular that of water. These studies put in place the basis for his critical paper on the electrolysis of water and provided a broad background for his future scientific activity. While in Italy his health improved, which gave him the impetus to pursue his goals.

*Theodor von Grotthusr*

## Grotthuss's Fundamental Paper

In the fall of 1805 at the age of 20, Theodor Grotthuss set about writing his first fundamental paper, on the electrolysis of water. Ttitled "*Mémoire sur la Décomposition a'l'Aide de l'Electricite Galvanique"* it was published in Rome in 1805. This paper distinctly presented a new approach to the explanation of the role of the electrical current during electrolysis, and some think it, in itself, could have been worthy of a Nobel Prize, if such had existed at that time. Years later Oswald translated this paper into German and made this strong comment (8):

> *Es ist die Schrift, durch die der Name Grotthuss vor allem berümt wurde, und die den grössten Einfluss auf die theoretischen Vorstellung über Elektrolyse ausgeübt hat*. (By this paper the name of Grotthuss will be very famous, and this paper has had a very, very great influence on the theoretical interpretation of electrolysis).

In this important paper, he explained why, during the electrolysis of water, hydrogen was generated at one pole and oxygen at the opposite pole, rather than throughout the whole solution as had been expected. This phenomenon, observed by A. Carlisle and J. W. Nicholson shortly after Volta's discovery of the pile, became known as the "Nicholson Paradox." It presented a challenge to scientists to explain satisfactorily this puzzling effect. It should be noted that, at the time of discovery of the pile by Volta, the conception of voltaic phenomena was based on the existing paradigm of static electricity, which in turn was based on the measurement of voltaic effects by electrostatic instruments.

Volta, by placing highly polished iron and copper plates in contact with each other (1799), had observed that these plates acquired opposite charges. This important observation led his contemporaries to believe that the electrical currents were of static nature as a result of the contact of the metal surfaces, which acquired opposite static charges. Thus, Volta stated that the galvanic and static fluids were identical.

John Baptiste Biot, in a well known summary report (Raporte) in 1803, tried to explain the generation of the electric current in a voltaic pile. He stated that the pile was generating two types of "fluids" which were electrostatic in nature because of the two different metals. He thought that insertion of the conductive pasteboard between the plates prevented the direct interaction of opposite fluids and allowed them to flow in opposite directions. The flow of current was perceived to be due to a chain of impulsive stimuli resulting in a large avalanche of short imperceptible discharges. Biot, even in 1824, did not appear to acknowledge the successive decomposition and recombination described by Grotthuss, Davy, and Berzelius, but attributed the effect to opposite electrical states of the portions of the decomposing substance at the poles.

Rene Just Haüy interpreted Volta's battery as being of purely electrostatic origin, believing that the constant current produced by Volta's battery was a result of a process of successive fast discrete impulses (9).

Grotthuss as a student in Paris stepped in at the time when the electrostatic model was the only way to explain the galvanic phenomena. He was able to recast established facts into a new perspective relating the chemical and physical phenomena. These original ideas presented by Grotthuss can best be understood by an examination of his original paper, which was translated into English and appeared in the *Philosophical Magazine in* 1806 (4). It is of interest to follow the ideas presented by Grotthuss, which have had such far reaching influence on the future research and that put to rest the electrostatic interpretation of the mechanism of voltaic battery.

In the first section of this paper "Action of Galvanic Electricity upon Certain .Bodies Dissolved in Water" Grotthuss set out to investigate the electrolysis of various salt solutions. In the opening sentence he sets the tone (10):

> Without wasting time on the discussion of the multitude of imaginary hypotheses invented to explain the decomposition of water by the electrometer apparatus, I shall give a general theory of the decomposition of liquids by galvanic electricity, which, in my opinion, brings the effects of the latter to a simple and satisfactory explanation.

He confirmed that certain metals were deposited at the negative pole (connected to the copper disc) and formed crystal growth in the direction of the galvanic current while oxygen was evolved at the positive pole, connected to the zinc disk. With metals that did not deposit at the negative pole, hydrogen was evolved; and at the positive pole a precipitate of oxide was formed. He observed that metals have different affinities, as was later observed by Davy and Berzelius. He stated (11):

> All metals in solution are not equally decomposed by galvanic electricity. From nitrate of manganese I obtained gaseous bubbles at the negative pole in place of a metallic deposit; and it seems that when in similar circumstances, the metal, in solution has more affinity to oxygen than hydrogen has for this principle, it is the water which alone suffers the decomposition.

In the case where the arborisation (deposition of metal) takes place at the negative pole, Grotthuss observed no gas evolution and concluded that (11):

> …either that hydrogen arising is combined with the oxygen of the metallic oxide, or that the action is only exercised upon this oxide and not upon the water. This last conclusion ought to be a true one; for we can scarcely admit that the hydrogen is able to carry off completely the oxygen from the oxides of zinc and iron, as well as from certain acids their solvents, in which these two metals are not dissolved, except after having produced an effect contrary to this admission, by decomposing water.

In addition Grotthuss states (12):

> When the current of galvanic electricity acts upon water either pure or when charged with some soluble substance, the positive pole attracts the *oxygenating* principle, while the negative pole attracts the *oxygenated* principle of the liquid. If the proportion of the components at the latter is variable, it becomes oxygenated at the extremity of the wire in communication with the disk of zinc, and deoxygenated at the extremity of the wire in contact with the disk of copper.

Grotthuss perceived that the battery acted not only as a galvanic generator, but also as a dynamic polarized system composed of particles; i.e., molecules of opposite nature as an extension of the pile.

In the second part of the paper, titled "Theory of the Decomposition of Liquids by Means of Galvanic Electricity," Grotthuss attempted to resolve and to reconcile the views of previous researchers with the theory of the nature of water. He states (13):

> It is first necessary to know if the two products of the galvanic poles come from one and the same molecule of water, or rather from two different molecules; and in the latter case we may ask what becomes of the hydrogen at the place where oxygen is perceived? And in return, what becomes of the oxygen where hydrogen is perceived?

Volta's pile as well as the philosophical ideas presented by Schelling and by others probably gave Grotthuss the idea to develop the concept of polarization. He states (14):

> The column [pile] of Volta, which will immortalize his name, is an electrical magnet, every element of which (i.e. each pair of disks) possesses its negative and positive pole. The consideration of this polarity suggests to me the idea that it might establish a similar polarity among the elementary molecules of the water solicited [attacked] by the same electrical agent; and I confess that this afforded me a spark of light on the subject… Thus, when the galvanic current traverses a quantity of water, each of the two component principles of the latter is solicited [attacked] by an attractive force and by a repulsive force, of which the centers of action are reciprocally opposite, and which, by acting in the same manner, determines the decomposition of this liquid.

In addition, Grotthuss observed that the molecules of water were affected by the action of attractive and repulsive forces in the direction of the galvanic current. The reciprocal action of elementary molecules in contact resulted in recombination, and only terminal water molecules underwent electrolysis. In an illustration in this paper [p 336] he showed that water molecules are polarized in the presence of a galvanic current. Although the molecular formula of water had not been established, it was known that water was composed of two elements—oxygen and hydrogen and that oxygen was more negative than hydrogen. Grotthuss stated (15):

> At the moment of establishing a current of galvanic electricity in this water, the electrical polarity mani-

> fests itself among its elementary molecules in such a manner, that the latter seem to constitute the complement of the pile in action.

In summary, this paper presented an original explanation of the electrolysis of water. This explanation postulated that during electrolysis, the molecules of water and salt were polarized and formed polar chains into a unified system. Thus the polarized molecules became the continuation of the copper-zinc couples constituting the pile. He further explained that under the influence of the electrode poles, there formed, in parallel lines in the solution, polarized molecular chains whose members at each end were discharged at the opposite poles. The water molecules touching the electrodes split into the component parts of the water molecules. Thus, at the negative electrode, hydrogen gas was evolved, while oxygen was evolved at the positive pole.

The water molecules continuously exchanged their component parts between their nearest neighbors as well as with surrounding members of the chain. This also meant that leaping interactions were proportional to the transfer of electrical fluid in the microscopic world and that it proceeded in discrete and finite portions. This exchange took place by relays along the molecular chains suggesting the idea of a leap-frog interaction that arose from the transfer process during electrolysis along parallel lines. [Faraday, using Grotthuss's model some forty years later, developed the force line model. (16).] Furthermore, this line of thought led to a concept resembling ionization. In addition, the concept of leaping interactions led to a principle of atomism, discreteness of material objects, divisibility, and a change from static structure to a dynamic representation of matter. The majority of the scientific community accepted the electro-conductivity mechanism proposed by Grotthuss.

For his contribution to the theory of electrolysis he was elected an honorary member of the Galvanic Society of Paris in 1808. The same year he was named a corresponding member of the Turin Academy, and in 1814 he was elected as a corresponding member of the Munich Academy. These high honors were granted to Grotthuss, while he was in his early twenties, despite the fact that he had no formal diploma from any university. Even though the greater part of the scientific community recognized his contribution, some chose not to give credit to Grotthuss. There were prominent researchers such as Davy, who used Grotthuss's original ideas in developing chemical affinity theory, and Berzelius, a proponent of electro-chemical dualism, who never mentioned Grotthuss's original paper in his 1823 chemistry textbook. [Berzelius merely cited him in a minor contribution. (17)]

Davy, in a publication a year and half after the original publication (18), again took the ideas of Grotthuss without giving him credit. In fact, Grotthuss stated that Davy took his paper and left out his drawings. Some 30 years later, in a reference to Davy's work Faraday tried to correct matters by stating (19):

> He mentions the probability of succession of decompositions and recompositions throughout the fluid, agreeing in respect with Grotthuss and supposes that the attractive and repellent agencies may be communicated from the metallic surfaces throughout the whole of the menstruum being communicated from one particle to another particle of the same kind.

The qualitative mechanism of electrolysis of liquids presented by Grotthuss influenced Faraday in his electrochemical studies. Faraday, in his publications (as summarized in Experimental Researches in Electricity) recognized Grotthuss's original contribution on the electrolysis of liquids, and by quoting this work he restored it to the mainstream of research. Grotthuss's original paper provided Faraday with valuable ideas, as indicated in his analysis of the Grotthuss's original paper (20):

> Grotthuss, for instance, describes the poles as centres of attractive and repulsive forces, these varying inversely as the squares of the distances, and says, therefore, that a particle placed anywhere between the poles will be acted upon by a constant force. But the compound force, resulting from such a combination as he supposes, would be but anything but a constant force; it would evidently be a force greatest at the poles, and diminishing to the middle distance. Grotthuss is right, however, in the fact, according to my experiments, that the particles are acted upon by an equal force everywhere in the circuit…but the fact is against his theory, and is also, against all theories that place the decomposing effect in the attractive power of the poles.

Some 40 years later, Faraday confirmed Grotthuss's original polarization concept in an experiment with small pieces of silk threads that became polarized and aligned in solution during electrolysis.

## Grotthuss's Investigations at his Home Laboratory (1808-1812)

In 1808 Grotthuss left Paris and on his return to his home estate he stopped at Munich, where he met A. F. Gehlen, the famous German editor of *Physik, Chemie und Mineralogy*. His acquaintance with Gehlen enabled him in later years to publish his original works and to keep contacts with other scientists. Upon returning to his mother's estate, Grotthuss continued to work feverishly in his home laboratory. He acquired glassware from the neighboring apothecary, his childhood friend, Bidder. He built needed equipment such as galvanometers and volumetric flasks for the gas volume measurements. He worked enthusiastically as a hermit far away from scientific communities, having only an occasional contact through journals and correspondence. He regretted not being able to be in direct contact with other scientists except by mail, which was slow and often subject to loss. Periodic bouts of an inherited stomach ailment hampered his work. In the period 1808-1822, while in his mother's estate, Grotthuss carried out numerous studies. During his lifetime he published 76 papers on original research, observations, and proofs, most of which appeared in Western European journals. Some of his very important papers, published in Eastern European journals. were rediscovered after his death.

In 1805, in Naples, he joined von Humboldt and Gay Lussac, who studied volcanic gases and investigated the effect of pressure on the course of gas mixture reactions and at what degree of rarification detonating mixtures would cease to ignite (21). Grotthuss, on his return to Paris (1808) and to his estate (1808-1812), pursued the studies of flames of gas mixtures such as oxygen and hydrogen and other gas mixtures (22-24). He made a fundamental observation that the mixture of gases in narrow tubes will not ignite.

In 1816 Sir Humphry Davy, while studying the mixtures of hydrocarbon gases with oxygen, showed that flames could not pass through narrow tubes, as had been previously reported by Grotthuss. He came upon the idea of screening flames in the lamp with a metallic screen and thus developed the miner's safety lamp—without giving credit to the previous work of Grotthuss. Stradinš, a member of the Latvian Academy of Sciences, in his extensive historical review described the discovery of the miner's safety lamp and Davy's references to Grotthuss (25). In his lecture before the Royal Society in 1817 Davy, for the first time, named Grotthuss as his predecessor in this field; in the same year, however, he stated that his conclusions were very different from those presented by Grotthuss.

Grotthuss responded to Davy's criticism (26):

> Mr. Davy in his paper on flames … mentions me only when he tries to refute or correct my findings on conclusions, at the same time, when he confirms them he takes for himself not only the suggestions of my experiment, but even the phenomena which I had found much earlier than he.

L. W. Gilbert, the editor of the *Annalen der Physik und Physikalische Chemie*, in a letter to Grotthuss dated April 28, 1818, which was found in the archives of Kurland Provincial Museum and published by O. Clement, described the grievances of Grotthuss (27):

> It is incomprehensible how such an honorable man as Davy can have so little fairness and so willingly appropriate everything.

## The Last Ten years of Grotthuss Life: 1812-1822

The war between France and Russia (1812) disrupted Grotthuss's normal work, but it enabled him to establish new contacts in St. Petersburg and to open new research opportunities. Before Napoleon's occupation of the region Grotthuss spent six months in St. Petersburg, where he became a friend of A. F. Scherer, a member of the St. Petersburg Academy of Sciences. Scherer provided him with some phosphorescent crystals that influenced Grotthuss in the studies of light and phosphorescence. A founder of the journals *Allgemeine nordische Annalen der Chemie* and *Allgemeine nordische chemische Blätter.* Scherer devoted a considerable amount of space to contributions by Grotthuss in these publications. They described in detail Grotthuss's research dealing with phosphorescence, the influence of alkalis on the electrolytic conductance, and the chemical interaction of light and electricity. Because these publications were not widely circulated in Western Europe, some of his research results were rediscovered and recognized only after his death. Grotthuss published some of his research results in the journals edited by Gehlen, J. E. Gilbert, J. B. Trommsdorff, and J. S. C. Schweigger. In his journal Schweigger included Grotthuss along with the names of Berzelius, H. C. Oersted, T. J. Seebeck, and other famous scientists. Schweigger also published a collection of Grotthuss's proportional weight and material tables, which were widely used by chemists and pharmacists.

After his stay in St. Petersburg Grotthuss returned to the estate, where he continued his research, in particular in the areas of electrolysis and interaction of light. Professor G. F. Parrot at the Dorpat University, Estonia, offered Grotthuss the position made available after the retirement of his associate, Grindel, in 1814. The University Appointment Committee voted by a great majority (15 to 2) to offer the professorship to Grotthuss, who was deeply touched. He was reluctant, however, to commit himself for six years of service because of his health. The final approval of this position would have had to come from Moscow, where it got sidetracked for political reasons.

Grotthuss then joined the activities at the Peter's Academy in Jelgava (Mitau), close to his mother's estate. Here he became an active member of the Kurland's Literature and Arts Association, where he presented papers on research and shared various views with the association members. His papers and those of E. Echwald, M. G. Paucher, K. F. Gauss, and others were summarized in two books published under the auspices of the Peter's Academy. Here he worked closely with his childhood friend Bidder, a well established pharmacist. Heinrich Rose worked in Bidder's apothecary in Mitau from 1816-1819. Here he met Grotthuss and carried out electrolysis experiments of metal ion solutions as guided by Grotthuss. In 1820 Rose contributed a paper titled "Über die Theorie Metallreductionen des Herrn Grotthuss" to the collection of research papers by Grotthus, which appeared in *Physisch-chemische Forschungen* in 1820. Thus, it appears that Grotthuss had a great influence on Rose.

In this period Grotthuss formulated some original ideas pertaining to the absorption of light, which included phosphorescence, fluorescence, and photochemical reactions. He was interested in the physiological aspects of chemical interactions of light with polarized molecular particles. He at first accepted Newton's model of light. However, after studying the crystals exhibiting phosphorescence in 1812, he observed that the phosphorescent light was different from the absorbed light, which was contrary to Newton's mechanistic theory. He concluded that the phosphorescence phenomenon was associated with the motion of light and the structure of the body being irradiated. He proposed that the light at the surface of the fluorescent crystal split into +E and –E components, which, upon interaction with polarized molecules in the crystal, were separated and caused the emission of light of a different color from that used for irradiation, Grotthuss concluded that interaction of light with matter causes specific motions characteristic of colors and thus can dampen or enhance different colors (28). In so doing, he presented the theoretical foundations for luminescence, which were later elaborated in the second half of the $19^{th}$ century by A. E. Becquerel, D. Brewster, and A. D. Stokes.

In 1818 Grotthuss attempted to develop a unified electromolecular concept of physical and chemical phenomena, and published a paper "Über die chemische Wirksamkeit des Lichtes und der Elektrizität" in 1819 (29). Here he proposed that the combination of different types of electricity (+E and –E) produces heat; and, if the combination of different kinds of electricity is prevented by the atmosphere or an insulating layer, the light is emitted—the color of which is determined by its vibrations. He concluded that "+E and –E" are the original [energy] sources for light, heat, and electricity, which are different modes of [energy] manifestation. In the last part of this paper he elaborated on his ideas presented in the first paper dealing with the electrolysis of water. He stated that in solution even without electrical current there is a continuous exchange between molecules and their elementary parts. These are closed circles of exchanging charged entities (30). This cannot be observed in solution because of the established equilibrium between electrical forces. An external force destroys the equilibrium and closed circles are opened. Molecular chains are formed and are stretched between the poles. At the end of the chains, at the poles, the cascading molecular elements of water molecules are separated. Here also Grotthuss proposes that in solution there exist molecular fragments. Fifteen years later Faraday, in presenting his electrolysis theory, established these fragments as being ions. In studying the tendency of metals to be oxidized or reduced during electrolysis, Grotthuss concluded that –E in all metals is chemically bound. We quote this powerful statement verbatim (31):

> Auf jedem Fall halte ich es für gewiss das alle Metalle –E chemisch gebunden enthalten… [In every case I hold it for certain (I am firmly convinced) that all metals contain a minus E which is chemically bound.]

Almost 80 years later in 1895 J.J. Thompson established the presence of the electron as a basic component of nature.

In the study of iron (III) thiocyanate alcoholic solutions, Grotthuss observed that the solution faded when exposed to light and that the rate of fading was proportional to the duration of the exposure and the intensity of the light. Consequently, in the study of thiocyanate and cyanide complexes of iron (III) and cobalt (II) he discovered the basic laws of photochemistry: that the photochemical reaction could be caused only by the light absorbed by the substance and its rate was proportional to the time of exposure and to the intensity of the light. These observations by Grotthuss were confirmed some 20 years later by J. F. W. Herschel and J. Draper. Eventually, these conclusions became known as the Grotthuss-Draper first and second laws of photochemistry. Some think that these studies in the field of photochemistry would have been worthy of a Nobel Prize if such an award had existed at that time.

Grotthuss pursued research in many areas outside of electrolysis and interaction of light with matter. He synthesized potassium thiocyanate salts of iron, mercury, silver, and gold by fusion of sulfur with the corresponding cyanide salts. He separated iron (III) chloride from manganese (II) chloride by taking advantage of the solubility difference of these salts in alcohol. He also, at the request of the academician Scherer, who was collecting data on mineral springs in the Russian empire, analyzed the mineral springs in his neighborhood (Smardone). Here he used ammoniacal silver solution for the determination of sulfide rather than copper chloride as was customary at that time. While J. W. Goethe was investigating the sulfur sources in the mineral springs of *Bad Berka*, Germany, Grotthuss suggested that the reduced sulfur in mineral springs was the result of the reaction of organic matter with gypsum. He also analyzed the composition of the meteorite, Lixna, which had recently fallen in the estate of Liksna. He concluded that the meteorite was formed in a waterless environment.

Also, in the period 1816-1818 he studied the properties of thiocyanate and thiocyanic acid and developed analytical methods for iron (III) and cobalt (II). At this time Schweigger published a collection of Grotthuss's proportional weights and materials tables, which became widely used by chemists and pharmacists (32).

In his wide ranging investigations, he observed and reported the phenomenon of electrostenosis: namely, that silver dendrites were formed at the very narrow cracks of the glass at the anode because of an electrocapillary effect. This effect was rediscovered 70 years later and elaborated on by F. Braun (1891) and E. J. Kohen (1898), who called it electrostenosis.

In correspondence with Berzelius Grotthuss expressed a wish to work in the renowned Swedish chemist's laboratory, but his failing health prevented the fulfillment of his wish. He continued to work enthusiastically in spite of his failing health and increasingly painful setbacks. In the last year of his life, he was disappointed and felt left out of the main stream of the scientific community. As a result of great suffering, he committed suicide on March 20, 1822 at the age of thirty-seven. He was buried in his mother's estate. However, after the estate was sold to new owners, Grotthuss remains were moved to a new resting place which is unknown. It can be said that even at the moment of his death he searched for the secrets of nature and thereafter he has remained a beacon of light. As he wrote (33):

> Lux lucet in tenebris quamvis nihil obscurius luce. [A literal translation: Light shines in darkness, however, nothing darkens the light.]

## Reverberations after Grotthuss's Death and Rediscovery of his Works

Bidder, a life long friend, commented after Grotthuss's death, that in the last years of his life Grotthuss worked sporadically, and that he made a number of rash statements because of his lack of energy to carry out necessary experiments (34). As time passed, his physical existence became more and more difficult for him to bear. Before his death he commented to his friend (34):

> What is the value of a sad life, if I am not able to work and if I dwell only on my errors?

He left his archives and the library to Peter's Academy in Jelgava. By freeing his serfs in his will, he went against the accepted norm of the Kurland high society. His will was contested, and the Kurland Literature and Art Association declared that Grotthuss was mentally ill. Ironically, at one time time he was one of its most prominent members. His will was annulled. With this action, the Grotthuss family and the Kurland high society closed the chapter on the life of Theodor Grotthuss, who dared to challenge the established code of society. Yet as the family tried to forget this episode, his contributions to science sustained his memories and survived the trials of time.

Almost a century later in 1906 his fellow country man, the famous scientist and editor, Wilhelm Ostwald, dedicated a special edition, compiled by Luther and Ottingen, of *Ostwald's Klassiker der exakten Wissenschaften, Nr.152* to Grotthuss. Ostwald commented (35):

> Grotthuss war ein Forscher mit ausserordentlich stark ausgebildeter wissenschaftlicher Phantasie, und so ist es erklärlich, daβ manche seiner Ahnungen sich nicht verwirklicht, manche seiner Beobachtungen sich als unrichtig erwiesen hat. Immerhin geht es auch bei seinem kühnsten Spekulationen stets von experimentellen Tatsachen aus, und seine erkentnis-theoretischen Anschaungen klingen häufig an die Kirchoff-Machsche Theorie der Wissenschaften an. [Grotthuss was a researcher of exceptionally well developed scientific vision, and it is obvious that some of his perceptions have been shown incorrect in respect to some of his observations. However, there are in his ingenious speculations always experimental facts, and his perceived theoretical insights resonate repeatedly with Kirchoff-Machsche theory.].

It is interesting to note that Arrhenius in his Nobel Prize lecture in 1903 echoed a view very similar to that presented by Grotthuss a century earlier (36):

> The general tendency in scientific research appears to attach more and more importance to electricity, the most powerful factor of nature, and developments in this direction are now proceeding very rapidly.

Grotthuss in his paper of 1805 stated (37):

> The admirable simplicity of the law to which this phenomenon is submitted coincides, to our astonishment, with the laws of the universe. Nature can neither create nor destroy; since the number of bodies is never augmented or diminished, but all without exception are subject to mutual exchange of their elements; and when we consider the wonderful effects of electricity, which acts often in secret, although spread over the universe, we cannot refrain from pronouncing it to be one of the most powerful agents of grand operations of Nature.

In a lecture at the University of California in Berkeley in 1906 Arrhenius stated (38):

> No simple formula conveys the whole sense of structure of the hydronium ion in water because protons transfer rapidly one $H_20$ molecule to another…The explanation which is called THE GROTTHUSS mechanism is in the migration of the proton is in fact not an actual movement of the ion through the solvent but a cooperative rearrangement of the atoms: a proton jumps from one 0 atom to the next along a hydrogen bond, the receiving molecule becomes the cation, and one of its protons can now migrate to another neighbor in the same way. The migration is a cooperative process that takes place through a network of several hydrogen bonded $H_20$ molecules.

The Lithuanian and Latvian Academies of Science in the period of 1960 to the present have undertaken extensive investigations of Grotthuss's contributions to science and have organized special conferences dealing with his life and scientific works. In 1994 the Lithuanian Academy of Science and von Grotthuss family established a special fund to support further investigations into Grotthuss's life. Also, in 1997 in Germany there was established the Förderverein T.v. Grotthuss. The contributions of Theodor Grotthuss have cast his imprint on many large areas of science for over two centuries, and his light is still shining brightly in the darkness.

## REFERENCES AND NOTES


1. C. J. T. Grotthuss, "*Mémoire sur la décomposition de l' eau et des corps, qu' elle tient en dissolution a' l' aide l' électricite galvanique*," Rome, 1805.
2. C. J. T. Grotthuss, *Ann. Chim. Phys. (Paris)*, **1806**, *58*, 54-74.
3. C. J. T. Grotthuss, *Repertory of Arts*, **1806,** 9, 365-370.
4. C. J. T. Grotthuss, "Memoire upon the decomposition of water, and of the bodies which it holds in solution by means of galvanic current," *Tillochs Philos. Mag.*, **1806**, *25*, 330-339.
5. A. Volta, "On electricity exited by mere contact of conducting substances of different kinds, *Philos. Trans. R. Soc. London*, **1800**, *90(2),* 403-430.
6. J. A. Krikštopaitis, *Pralenkęs Laiką: Theodor Grotthuss*, Philosofijos ir Sociologijos Institutas, Pradai, Vilnius, 2001, 181. Note: This book was a primary source and provided extensive biographical information pertaining to Grotthuss; also, *Ostwald's Klassiker der exakten Wissenschaften,* No 152, Engelman, Leipzig, 1906, provided reprints of the papers.
7. Ref. 6, p 12.
8. R. Luther, and A. v. Ottingen, *Abhandlungen über Elektricität und Licht von Theodor Grotthuss,* Engelman, Leipzig, 1906 (*Ostwald's Klassiker der exakten Wissenschaften*, No 152, 1906, *191*).
9. "Attaque par une succession rapid le petites impulsions," *Trait èlémentaire de physique*, Paris, 1803, 53.
10. Ref. 4, p 330.
11. Ref. 4, p 331.
12. Ref. 4, p 332.
13. Ref. 4, p 334.
14. Ref. 4, p 335.
15. Ref. 4. p 336.
16. W. L. Pierce, *Michael Faraday,* Chapman and Hall, London, 1965, 357.
17. Ref. 6, p 177.
18. H. Davy, *Philos. Trans. R. Soc. London*, **1807,** *98*, 29-42.
19. Faraday's Select Researches in Electricity with Appreciation by Professor Tyndall; Everyman Library, in Ernest Rhys, Ed., *Experimental Researches in Electricity by Michael Faraday, D.C.L. & F.R.S,* J. M. Dent & Sons Ltd, London, Toronto; E. P. Dutton & Co, New York; first published 1914, 51, 219.
20. Ref. 17, pp 63, 235.
21. *Ostwald's Klassiker der exakten Wissenschaften*, No 42, Engelman, Leipzig, 1893.
22. T. v. Grotthuss, *J. Chem. Phys.,* **1809.** *9,* 245-260.
23. T. v. Grotthuss, *Schweiggers J. Chem. Phys.*, **1812 ,** *4***,** 238-258.
24. T. v. Grotthuss, *Schweiggers J. Chem. Phys.*, **1813**, *9***,** 327-337; *Scherer's Nordische Blätter für Chemie,* **1813,** *1*, 101-113.
25. J. Stradinš, *Chymia,* **1964,** *9,* 127-145.
26. T. v. Grotthuss, *Gilberts Ann. Phys.,* **1818**, *58,* 345-369.
27. O. Clement, "Vom Chemiker Theodor Grotthuss," *Archiv für Geschichte der Natur, Wissenschaften und der Technik*, Leipzig, **1916,** *7,* 387.
28. T. v. Grotthuss, *Schweiggers J. Chem. Phys.*, **1815,** *14,* 163,174.

29. T. Grotthuss, "Über die chemische Wirksamkeit des Lichtes und der Elektricität," *Jahres Verhandlungen der Kurländischen Gesellschaft für Literatur und Kunst,* **1819,** *1*, 119-184.
30. Ref. 27, p161.
31. Ref. 27, p 171.
32. T. Grotthuss, *Verbindungsverhältnis*, Nürnberg, 1821**.**
33. Grotthuss seems to be saying, "My light is shining in darkness but nothing can obscure that light. "
34. H. Bidder, "Auch Theodor von Grotthuss ist nicht mehr," *Allgemeine nordische Annalen*, **1822**, *8*, 106.
35. *Ostwald's Klassiker der exakten Wissenschaften,* No 152, Engelman, Leipzig, 1906, 194.
36. S. Arrhenius, "Development of the Theory of Electrolytic Dissociation," *Nobel Lecture: Chemistry*, 1901-1921, Amsterdam, 1966, 58.
37. Ref. 4, p 339.
38. *Chemistry Being Lectures Delivered at the University of California in Berkeley, Svante Arrhenius,* Longman, Green and Co, New York, 1907.


## ABOUT THE AUTHORS


Bruno Jaselskis, Professor Emeritus of Chemistry at the Loyola University of Chicago was born in Lithuania. After World War II he worked in Germany for UNRRA (United Nations Relief and Rehabilitation Administration) and the World's YMCA. In 1949 he immigrated to the United States and received the B.S. degree in chemistry from Union College, Schenectady, NY and the M.S. and Ph.D. from Iowa State University. After 1956 he pursued a teaching career at the University of Michigan and then at Loyola University. His primary research interests are in the area of analytical and noble gas chemistries and historical developments.

Emeritus Professor Carl E. Moore was born September 25, 1915 in Frankfort, KY. He received the B.S. degree in chemistry from Eastern Kentucky State Teachers College in 1939 and the M.S. degree in chemistry from the University of Louisville in 1947. He entered the Ohio State University following WWII and received the Ph.D. in chemistry in 1952. He joined the faculty of Loyola University Chicago in 1952, where he rose through the ranks to Associate Professor, to full Professor, and eventually to Chemistry Department Chairman. He is still active in research and writing. His current interests are in analytical chemistry and history and philosophy of science.

Emeritus Professor Alfred von Smolinski was born in Cernauti, Romania December 7, 1919. He studied for three years at the Department of Chemistry of the University of Cernauti, transferred to the University of Bucharest for the final year, and received his diplom-degree in chemistry. In 1942 he moved to Germany and was employed in the chemical industry. In 1955 he immigrated to Chicago and received the M.S. and Ph.D. degrees from Loyola University Chicago. Later he taught at Youngstown State University and at the University of Illinois Chicago in the Department of Medicinal Chemistry.