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# Capillary Electrophoresis (CE) and its Basic Principles in Historical Retrospect. Part 3. 1840s –1900ca. The First CE of Ions in 1861. Transference Numbers, Migration Velocity, Conductivity, Mobility

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**Abstract.** Since electrophoresis is a physical phenomenon – it is the movement of dispersed charged particles relative to a liquid under the influence of a spatially uniform electric field – its history is not limited to its use as a separation method. The history of capillary electrophoresis in particular, i.e. electrophoresis in capillary-sized open tubes, therefore does not begin in the 1960s, as is commonly assumed, but already a century earlier, if one refers to its principles. Capillary electrophoresis of ions was first performed by the French physicist Edmond Becquerel in 1861, about the same year as that of colloidal particles. Becquerel owns therefore the priority. It was subsequently performed on three other occasions in the *Long Nineteenth Century*, by Wilhelm Beetz in 1865, by Wilhelm Ostwald and Walther Nernst in 1889, and by Friedrich Kohlrausch and Adolf Heydweiller in 1895. All of these experiments were carried out in the context of research on conductivity and ion migration. Based on the theories of Grotthuß, Davy, and Faraday, it was believed until the 1840s that both the anions and the cations of a dissolved strong electrolyte – to which this review refers – migrate at the same velocity or speed in an electric field, but experimental observations in the mid-1840s cast doubt on this view. Wilhelm Hittorf was the first to show that these ions could migrate at different speeds, still consistent with Faraday´s laws. He was able to prove his hypothesis with experimental data and determined the migration velocities of the two types of ions in an electrolyte relative to the sum of their velocities, which he termed "Überführungszahlen" (transference or transport numbers). However, they did not initially yield the absolute velocities of the ions. This was achieved later by F. Kohlrausch, who devoted four decades of his research life, namely from the end of 1860 to about 1910, to the study of the conductivity of electrolyte solutions and the migration of ions. He discovered in 1879 that ions move independently from each other in solution (1st Kohlrausch law). It is remarkable that until the late 1880s it was generally believed that free ions do not exist in solutions in the absence of an external electrical force, but that ions were always tightly bound to their counterions. This belief dated back to Grotthuß in 1805. Although Rudolf Clausius hypothesized in 1857 that free ions are actually present in solutions as result of their thermal motion, this did not find further resonance. It is also remarkable that during this whole period under consideration no attempt was ever made to separate ions with the same charge, although their different migration properties were already known. Continuing his research, Kohlrausch found empirically in 1900 that at extremely low concentrations the molar conductivity of ions, i.e. the conductivity related to their concentration, is a function of the square root of their concentration and approaches a certain limit at infinite dilution (2nd Kohlrausch law). As a precursor to this law, he derived in 1885 for larger concentration ranges the little-known relationship of molar conductivity as a function of the cubic root of concentration. He calculated the migration velocities of ions from their conductivities and characterized the migration behavior by their mobility, which is a central property in electrophoresis. Kohlrausch was certainly a formative investigator of the electrophoretic properties of ions, but his work focused mainly on strong electrolytes. This review covers the research results in the field of mainly this class of electrolytes in the period from 1840 to about 1910; but it also reports on the personal background of some researchers who, despite important contributions, have been unjustly forgotten, as well as on researchers who were active outside the scientific community. Mention is made, for example, of Gustav Theodor Fechner, who was the first to prove the fact, indispensable for electrophoresis, that Ohm´s law also applies to electrolyte solutions. However, in contrast to the generally applied results of his investigations, he himself was rather ignored by later researchers. The conductivities and electrophoretic properties of weak electrolytes, which were known to Kohlrausch and his contemporaries but hardly explicable to them, at least until 1884, are not discussed in detail in this review. In that year, Svante Arrhenius published his groundbreaking theory of electrolyte dissociation as his dissertation. This theory and the resulting consequences for the whole subject of electrolyte solutions require, however, a separate historical retrospect.

**Keywords:** first capillary electrophoresis, ions, strong electrolytes, Hittorf, Clausius, Kohlrausch.

## INTRODUCTION

Although the motion of dissolved charged particles by electrophoresis[1] during electrolysis was the topic of Part 2 of this series[4] the magnitude of their migration velocities was not subject of discussion.[2] That part covered the period from the first observations of electrolysis and the inextricably linked electrophoresis in 1800, and the assumption that electrical forces from the electrodes exert on the ions by action at a distance. This concept was superseded in the mid-1830s by Michael Faraday's pioneering theory that ions move at electric lines of force, which led to James Clerk Maxwell's field theory.[5] At the time when the action at a distance was widely accepted, the migration velocity of the ions was believed to vary with their distance from the electrodes, while as consequence of the field theory the assumption of a constant velocity prevailed. In no case, however, was the magnitude of the velocity of ion migration addressed. This will be the subject of this Part 3.

In short, and just for the sake of historical completeness, we mention the first attempt to measure the migration velocity by Peter Mark Roget,[3] which he already undertook in 1807. Roget tried to determine the migration speeds of oxygen and hydrogen generated by the electrolysis of water,[4] but without success, as described in refs. [6, 7], Chapter *Galvanism*, p. 30. Michael Faraday then took up the subject only in 1833 in the *Fifth Series of Experimental Researches* (refs. [8, 9]; 524. – 535.). In the *Eighth Series*[10] from 1834 he explicitly argued that both the anions and the cations of an electrolyte travel at the same speed in opposite directions at the electric lines of force, and based this assumption on the law of the definite electrochemical action. He argued that equal chemical equivalents of oppositely charged ions are required at their respective electrodes at the same time, otherwise electrolysis cannot happen. We discussed this point already in Part 2.[4]

Faraday briefly returned to the subject of migration velocities of particles in solution in 1838 in the *Thirteenth Series*.[11] At the end of this article he reviewed earlier attempts to measure the speed of electricity in metallic conductors, which had been unsuccessfully carried out by William Watson in London in 1747 and 1748.[12, 13] That of light was carried out (with some success) by Charles Wheatstone in 1834.[14] Faraday himself speculated on an approximate velocity of the ions in solu-

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[1] To avoid misunderstandings, we indicate how we define electrophoresis. It is not just the migration of particles in an electric field, which, like colloids, have an electric double layer. Nor is it just the powerful separation method in use today, whose overwhelming importance, for example, for genomics, proteomics, metabolomics, and numerous other important areas we highlighted in Part 1.[1] It is in principle, as Hanns Lyklema most generally defined it, "*the movement of dispersed particles relative to a fluid under the influence of a spatially uniform electric field*".[2][3] We therefore have every reason to call such migrations electrophoretic (see also Part 2 of this series).[4]

[2] It should be noted in advance that the present part of our historical review deals mainly with single pure strong electrolytes in free solutions.

[3] The British physician Peter Mark Roget (1779, London – 1869, West Malvern, Worcestershire) was Fullerian Professor of Physiology an der Royal Institution from 1834 till 1837.

[4] Roget tried to measure the time interval between the closing of the electric circuit and the appearance of the gases on the separate electrodes, which were 46 inches (i.e., ca. 117 cm) apart. After the completion of the circuit, however, no measurable interval could be determined; a result which was predicable taking into account the already known theories of Grotthuß and Davy.

tion, (ref. [11], pp. 164, 165) but only vaguely.[5] In none of his contributions, however, Faraday reported on values of the migration velocities.

The assumption of equal ion velocities was challenged by Frederic Daniell and William Allen Miller by contradictory results of the electrolysis of copper and of zinc sulfate solutions in a double membrane cell, i.e., a cell divided by two diaphragm. After electrolysis, they found the same amount of copper in the cathode compartment as was initially put in. The amount of reduced copper plus the quantity that remained dissolved was exactly that as before electrolysis. From this, they concluded that the copper ions do not migrate and only sulphate traverses the entire distance between the electrodes. They hypothesized that the flow of the electrophoretic current[6] was mainly by the anions, while the cations contributed little.[15, 16]

Claude Servais Pouillet observed a similar effect in 1845 when he electrolyzed a solution of gold chloride.[7] He used a U-shaped tube with one of the electrodes in each arm. After passing the current, he found almost no gold in the arm with the negative electrode, but gold in its initial content in the one with the positive electrode. Pouillet concluded from this result that the negative electrode took up the gold, while the chloride was transported to the positive electrode through a series of decompositions and recombinations and was set free there. Like Daniell and Miller, Pouillet concluded that the migration velocities of the anions and the cations are not the same, contrary to previous belief.[19, 20] Alfred Smee[8] had a different point of view. He assumed that the primary process is the decomposition of water when a metallic solution (i.e., a solution of a salt of a metal) is subjected to galvanic action. The following reduction is a secondary process caused by the hydrogen produced first by the metal from its salt solutions.[21, 22] In summary, all experiments reported so far have led to different and contradictory assumptions about the electrophoretic migration velocities of ions but none has contributed to the central question of their magnitude.

However, before continuing the discussion of further approaches to determining the ion speeds, initiated by Wilhelm Hittorf and his concept of the transference number, the author will not fail to show that theories long believed to have been overcome still had ardent supporters in the middle of the *Long Nineteenth Century*, albeit rarely. At that time, it came as a surprise that established theories, e.g., those of M. Faraday, were still rejected by staunch proponents of the Phlogiston Doctrine. One of these advocates was William Ford Stevenson (1811 – 1852), after all Fellow of the Royal Society, who in 1846 published a book whose title already fully reveals its content. It reads "*Most important errors in chemistry, electricity, and magnetism, pointed out and refuted: and the phenomena of electricity, and the polarity of the magnetic needle accounted for and explained by a Fellow of the Royal Society*".[23] Moreover, Stevenson was so violently provoked by the award of the Gold Medal of the Royal Society to the noted physico-chemist William Robert Grove[9] in 1847 that he wrote a second conspicuously polemical book in 1849 entitled "*The Composition of Hydrogen and the Non-Decomposition of Water incon-*

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[5] The English apothecary, physician and natural philosopher Sir William Watson (London, 1715 – 1787) charged wires with electric machines in London in 1747 and 1748.[12][13] However, differences in the time of appearance of the discharges at the two extreme ties of a wire of 4 miles in length could not be determined visually. Charles Wheatstone attributed this miscarriage to the laggardness of the observing eye. He therefore constructed a device with rapidly rotating mirrors with which time intervals for the occurrence of electrically generated sparks could be measured beyond a millionth of a second. The measured velocity of light was either 576000 or 288000 miles per second, depending on the experimental circumstances assumed.[14] If we take the English mile, standardized in 1592 by the English Parliament as 1609 m, the latter velocity is about 460000 $km.s^{-1}$. Faraday himself attempted to derive an approximate value for the velocity of ions in solution, not of the action of electricity (nrs. 1651. and 1652. in the *Thirteenth Series*). It just ended with a hypothetical comparison of the quantity of electric power equal to the effect appearing instantly at the distance of 576000 miles from its source, on the one hand, with the effect which is obtained by the movement of hydrogen and oxygen after electrolysis of water through a certain distance of one tenth of an inch within an hour and a half, on the other hand.

[6] Our justification for coining the term *electrophoretic current* for the flow of charges carried by ions is given in detail in Part 2.[4] We emphasize that by *electrophoresis* we mean the movement of charged particles under direct current conditions, but not under alternating current conditions. Under both conditions the electrical conductivity nevertheless has the same values.

[7] Claude Servais Mathias Pouillet (1790, Cusance, Doubs – 1868, Paris) was a French physicist, and politician until the February revolution from 1848. His research comprised optics, photometry, thermodynamics and electricity. His main publications were, among others, the book "*Élémens de physique expérimentale et de météorologie*", published in 1827,[17] and "*Mémoire sur la chaleur solaire, sur les pouvoirs rayonnants et absorbants de l'air atmosphérique et sur la température de l'espace*"(*Memoir on the solar heat, on the radiating and absorbing powers of atmospheric air and on the temperature of the space*) in 1838.[18] Claude Pouillet must not be confused with his brother Marcellin Pouillet, who was chemist at *Conservatoire des Arts et Métiers*.

[8] Alfred Smee (1818, Camberwell – 1877, Finsbury Circus) was an English electro-scientist, metallurgist, chemist and surgeon.

[9] Sir William Richard Grove (1811, Swansea, Wales – 1896, London) was a Welsh advocate. He did not practice this job; instead he became interested in electrical phenomena, and published his first paper on this topic in 1838.[24] Grove improved the Voltaic battery and invented a fuel cell battery what he reported in 1839,[25][26] and which is named after him. A basically similar cell[27][28] was invented by the German-Swiss physicist and chemist Christian Friedrich Schönbein (1799, Metzingen – 1868, Baden-Baden).

*trovertibly established, in answer to the award of a medal by the Royal Society whereby the Contrary Doctrines are absolutely affirmed, also the Absurdity of the existing Systems of Electricity and Magnetism demonstrated and the True One Given*."[29] In this book, which, like his earlier one, was published by the author himself because all journals had refused to accept it, he again vehemently rejected all previous theories about the effect of electricity on liquids because they did not agree with the Phlogiston Doctrine. He was going so far as to accuse the Committee of the Royal Society, which awarded Grove the Golden Medal, of complete incompetence. We briefly quote verbatim one of his numerous attacks on the Committee, for example that on pp. 22-23.

> Every body must know that the appreciation of a paper upon a special subject, such as Chemistry, must *finally* depend upon the opinions and report of those gentlemen who are *presumed* to be specially acquainted with the subject. My observation must therefore be understood to apply exclusively to the COMMITTEE of Chemistry, and to no other portion of the Royal Society. Of the names of the gentlemen composing this committee I am at this moment ignorant, and I have no motive whatever to induce me to make the inquiry.
> I must, however, remark, that a TOTAL ABSENCE OF INFORMATION (a fact which will be elicited from a perusal of these pages) in a conclave of scientific men upon a subject on which they were *voluntarily* about to pronounce, and actually did pronounce, a most important opinion (an erroneous one, as may be supposed) pregnant with vast consequences is, I believe and trust without a parallel in the annals of science.[10]

To remind the readers of the state of science at that time, we mention that already more than four decades ago, *viz*. in 1804, the last prominent supporter of the phlogiston theory died, John Priestley, who defended this doctrine as late as 1803 with the book "*The Doctrine of Phlogiston Established and that of the Composition of Water refuted*".[30] We refer, on the other hand, to some contemporary works, e.g., those of Michael Faraday in 1846,[31] of James Clerk Maxwell´s first paper also in 1846,[32] of Rudolf Clausius and of James Prescott Joule in 1850,[33, 34] to name only the best known, and come to the works of Wilhelm Hittorf, who raised the knowledge of ion migration to a next level.

## W. HITTORF: RELATIVE MIGRATION VELOCITIES AND TRANSFERENCE NUMBERS OF IONS OF AN ELECTROLYTE

From 1853 to 1859[11] Wilhelm Hittorf developed a promising attempt to measure the migration velocities of ions.[12] He described his basic idea in 1853 in a first paper out of four, entitled "*Ueber die Wanderung der Ionen während der Elektrolyse. Erste Mittheilung.*"[36] (*On the migration of ions during electrolysis. First Notice.*)[13] This concept was still based on the traditional view that a cation, *C,* and an anion, *A,* are tightly bound in solution in the absence of an electric field, forming a single macroscopically uncharged unit or molecule *CA*. Consequently, free ions were believed not to exist. Note that in Hittorf´s conception the distance between the molecules was much larger than the molecules´ size. This differed significantly from the theories of Grotthuß, Davy and Berzelius, in which the molecules in the chains to which they arrange were in direct contact (see Part 2 of our series). This greater distance between the molecules is a precondition for Hittorf´s theory.

Hittorf based his concept on the relationship between the velocity of ions to their respective electrodes and the change in their concentrations there before and after electrolysis. Hittorf believed, in contrast to the established assumption of equal velocities, that ions migrate at different speeds, and postulated that this hypothesis can be confirmed by determining the change of their concentrations in their solutions at the electrodes by chemical analysis. He assumed that more of faster-moving cations must be found at the cathode and fewer of slower-moving anions at the anode, and vice versa.

In Hittorf´s concept the molecules *CA* with cations *C* and anion *A* are initially aligned under the influence of the electric potential, so that the ions are directed towards their respective electrodes, as shown in Fig. 1, row *a* (anions are depicted as black semicircles, cations

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[10] The capital letters and italics correspond to the original text.

[11] On November 24th of the same year 1859 Charles Darwin published his seminal book "*On the Origin of Species by means of Natural Selection, or the Preservation of favoured Races in the Struggle for Life*".[35]

[12] Johann Wilhelm Hittorf (1824, Bonn – 1914) studied mathematics und natural sciences in Bonn. After receiving his doctorate in 1848, he was given the position of a university lecturer in the following year. In 1856 he became professor of physics and chemistry at the University of Münster (Westphalia) and director of laboratories from 1879 to 1889. In the 1850s Hittorf contributed significantly to electrochemistry with the introduction of the transference numbers of ions, and constructed the instrumentations for their determination. Hittorf directed his research further to the passage of the electric current through gases and to the emitted spectra, and discovered the electron rays, later called cathode rays.

[13] The Engl. translation was published in *Harper's Scientific Memoirs* from 1899, ref. [37], pp. 49-80.

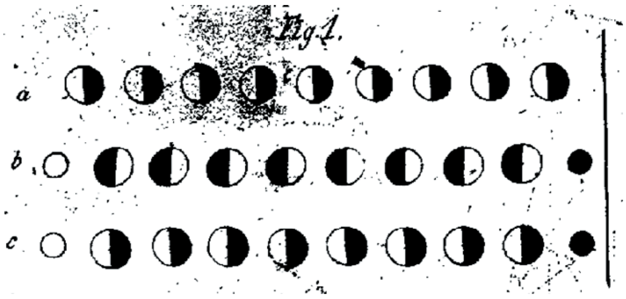

**Figure 1.** Hittorf´s concept and determination of the relative velocities and the transference numbers for the case that anions and cations have equal migration velocities. Anions: black semicircles; cations: open semicircles. In solution, the ions are present in pairs as macroscopically uncharged molecules, since all ions unite with their oppositely charged ions by electrostatic attraction. There are no free ions present. Row *a*: When an electric potential is applied, the molecules are aligned in the direction of their respective electrodes. Row *b*: The molecules are split into their ions, which migrate towards their corresponding electrodes, but reassemble with the oppositely charged ions in their immediate vicinity to form new molecules. Row *c*: The molecules rotate 180° to take the proper position in the field. Details can be found in the text. The figure is reproduced from Hittorf´s publication from 1853 (ref. [36], Plate II, after p. 352).

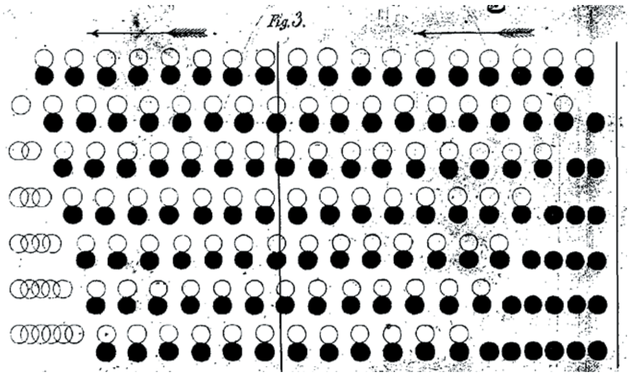

**Figure 2.** Hittorf´s concept and determination of the relative velocities and transference numbers for the case that anions and cations have different migration velocities. Anions: black full circles; cations open circles. Cations migrate in direction of the arrows to the left, anions to the right. Details are described in the text. (From ref. [36]).

as open semicircles; single-charged ions are considered). Next, the assembled ions of molecule *CA* separate from each other and move to the nearest oppositely charged ion,[14] with which they combine to form a new molecules *AC* (row *b*). Note that the ion travels as a free ion during the movement over this distance. Prior to the next step, this newly formed molecules *AC* had to rotate by 180° from *AC* to *CA* in order to get their proper position, that is to say, to be aligned with the respective electrodes (row *c*). Then, this process of decomposition and recombination continues as long as the electric potential is applied and the ions are finally decomposed electrolytically. The number of cations and anions decomposed by electrolysis is the same, independent of their velocities and in accordance with Faraday´s law of definite electrochemical action (see Chapter 3.1.4. in Part 2).

In order to prove the validity of his concept experimentally, a vessel of a measuring device was first filled with a solution with a given initial concentration of the electrolyte. In contrast to Daniell´s instrument, the vessel was not separated by a membrane, a diaphragm or another porous boundary. In Figure 1 the ions of the molecules are depicted as full and empty semicircles. If we suppose that the velocities of both ion species are equal, the ions reassemble into new molecules in the middle of their distance, and both travel along the same distance in a given time. Therefore, the change of their concentrations in their respective electrode compartments would be the same.

In the general case, when the two types of ions have different velocities, they travel different distances within a certain time before reuniting to form the next molecule. Then, eventually, more ions of the faster species reach the solution near the respective electrode, and fewer ions of the slower species reach the oppositely charged electrode. Thus, the number of ions of the two species in their electrode compartments is unequal. We emphasize again that this argument is valid even if, according to Faraday’s above-mentioned law, the same number of both ions is electrolytically decomposed in their compartments.

The question arises as to how Hittorf solved the problem of separating the vessel into an anode and cathode compartment without inserting a porous boundary. Hittorf’s solution, which circumvented this problem is shown schematically in Figure 2.[15] There, the electrolyte solution is separated not by a real boundary but by an imaginary one, indicated by the vertical line, which can be placed anywhere. The cathode is on the left side,

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[14] We called it counterion in previous Part 2, and will use this term in our publications. It is customary in modern phraseology.

[15] In this figure, the representation of the molecules in the vertical direction and in direct contact to each other is as in Berzelius’ paper, ref. [38], p. 278, is in discrepancy with Hittorf´s own assumption on p. 180, ref. [36] “*Der Zeichnung liegt die Annahme zu Grunde, daß die Entfernung zwischen den benachbarten Atomen des Elektrolyten größer als diejenige ist, in welcher die chemisch verbundenen Ionen jedes Atoms von einanander abstehen*“ (*The drawing is based on the assumption that the distance between the neighboring atoms of the electrolyte is greater than the distance between the chemically bonded ions of each atom.*) This requirement is satisfied in Figure 1. However, the deviation in Figure 2 has no consequence for Hittorf´s conclusions. [The author].

the anode on the right side. The cations are depicted as open circles, the anions as black circles. The transfer mechanism involving the 180° rotation is the same as described above. In the present example, the initial number of each ion type or equivalent is 18 (top row), The fictitious cathode compartment (left) contains 8 molecules, the anode compartment 10.

After completing the circuit, the ions migrate with velocities, *v*. In the case depicted in Figure 2 the cations cross the fictitious boundary faster than the anions. We assume, for example, that the anions travers ⅓, the cations ⅔ of their distance after their dispartment and the following recombination. But how can these different distances be determined? Hittorf turned this problem from the molecular to the molar scale, and developed the following method, for which we select at random the conditions in the anode compartment. He considered the change of the numbers (or equivalents) of anions and cations there. He recognized that from the begin of the electrolysis, shown in the top row, to its end (in the bottom row) the number of cations is reduced from 10 to 6, that is, 4 cations traversed the boundary and migrated towards the cathode. The number of anions in the anode compartment changed from 10 to 12, that is, it increased by 2. In the solution, 6 from the 12 anions remained and 6 were electrolytically decomposed; this decomposition applies to the cations as well. Thus, 2 anions crossed the boundary and moved into the anode compartment. To conclude, in the anode compartment a reduction of cations from 10 to 6 happened, equals 4, and the change of the number of anions is from 10 to 12, equals two. It follows that the change in equivalents in the anion compartment for the anions and for cations is ⅓ and ⅔. This result which would be obtained by experiment is identical to our input assumption.

Generally speaking, if the one ion traverses $1/n$ of the distance, the other $(n\text{-}1)/n$, after electrolysis the compartment of the former ion contains $1/n$ equivalent more of the one, and $(n\text{-}1)/n$ equivalents less of the other ion. Hittorf termed these numbers "Überführungszahlen" (transference or transport numbers) which we symbolize by $\tau$. Their sum $(\tau_+ + \tau_-)$ equals one. As mentioned above, they can be derived by quantitative chemical analysis of their concentrations.

The transference numbers express the migration velocity of the one ion relative to the counterion in a given electrolyte. The smaller the transference number of the ion, the slower is its migration velocity relative to its counterion. In the above example $\tau_-$ was ⅓, $\tau_+$ was ⅔, which is consistent with our initial assumptions about the different distance the two ions travel before forming a new molecule, or that the cation migrates at twice the speed of the anion. In general, the ratio of the transference numbers is equal to the inverse ratio of the velocities by $\tau_+/\tau_- = v_-/v_+$. It should be noted that one does not obtain the absolute migration velocity of an ion, but only that relative to the counterion of the same electrolyte.

It is also mentioned that the transference number expresses the fraction of current, *i*, transported by one type of ion in relation to the total current, i.e., the sum of the currents of both types of ions. It reads, for example, for the cation $\tau_+ = i_+/(i_+ + i_i)$. To get the currents Hittorf used a Poggendorff silver electrometer to simultaneously measure the total amount of current flowing during electrolysis and obtained $(i_+ + i_i)$. Then, he recalculated $i_+$ from the number of equivalents of the cation which he determined by chemical analysis in the anode compartment, and received the fraction of the current which was transported by the cation, and which is equal to its transference number $\tau_+$. Since $(\tau_+ + \tau_-) = 1$, the transference number, $\tau_-$, of the anion can be calculated without measuring it. It is therefore sufficient to measure the concentration, and thus the value of $\tau$, of only one ion in one compartment, and neither both in the same compartment, nor all four in the two compartments.

For the experimental determination of the concentrations of the ions after electrolysis, Hittorf modified the cell of Daniell and Miller by omitting the membranes. Readers interested in details are referred to the comprehensive description in Hittorf´s *First Notice* of 1853[36] which after all covers the three pages 187-189. The schematic drawing of the device is given in Fig. 4 in Plate II, after p. 352.

In this *First Notice* Hittorf examined different copper and silver salts. He found that their transference numbers were independent of the (low) current. Their changes, within the investigated temperature range between 4°C and 21°C proved to be unreliable.[16] Relevant for future research, especially for that of Friedrich Kohlrausch, was his observation that the transference numbers can depend significantly on the concentration of the electrolyte.

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[16] Note that we are discussing transference numbers, not conductivities. The German physicist Gustav Heinrich Wiedemann (1826, Berlin – 1899) observed that the electric conductance (or resistance) of electrolyte solutions depends on their viscosity. He varied the viscosity of the solution by varying the temperature and/or the salt concentration, and supposed a relation between the electric behavior and the mechanistic properties of the solutions. However, Wiedemann found that these conclusions were based on imperfect and preliminary experiments (see ref. [39], pp. 169, 170). Wiedemann´s conclusions nonetheless preceded Walden´s rule or Walden´s product (named after Paul Walden, a Russian-Latvian-German chemist), which he formulated in 1906,[40] sixty years after Wiedemann´s assumptions. Walden´s rule states that the product of the conductivity of an electrolyte solution at limiting conditions and the viscosity of the solvent is constant and independent of the solvent.

Hittorf also speculated on possible sources of error, primarily with respect to the role of water, since he assumed, contrary to popular belief, that instead of the cation of the salt, $H^+$ from the water could be reduced directly. However, he found that this primary, direct reduction of $H^+$ to gaseous hydrogen could be neglected. To support his opinion, he used solvents that were not decomposed electrolytically and measured the transference numbers in absolute ethanol and, in later Notes, in amyl alcohol. His results made it clear that water did not contribute to the current; it acted only as an electrochemically inactive solvent of the salts.

For the *Second Notice* from 1856 Hittorf constructed an improved device, again without membrane, and investigated whether or not electroosmotic flow affected the transference numbers.[41] He compared the results measured in devices with and without a membrane, and obtained the same transference numbers.

History showed that it is not uncommon for a front of critics and opponents to form when a new theory or method is introduced.[17] This also happened with Hittorf, and so he began his *Third Notice* in 1859[42] with a reply to Wiedemann´s critique.[39] Then a comprehensive reply to the derogatory reproaches [43, 44] of Gustav Magnus[18] followed, whom he called ”Hauptgegner meiner Arbeiten“ (main opponent of my works). In ref. [42], p.342, Hittorf wrote

> Magnus hatte in seiner ersten Abhandlung, §9, meiner elektrischen Arbeiten erwähnt und angegeben, daß dieselben mit der Zersetzung, welche die Elektrolyte durch den Strom erfahren, nichts zu thun hätten und über die Daniell´sche Theorie … nichts lehren. (Magnus had mentioned my electrical work in his first paper, §9, noting that it had nothing to do with the decomposition of electrolytes by the current and that it taught nothing about Daniell's theory.)

The rigor with which Hittorf rejected this criticism is evident in the fact that it extended over twenty printed pages. The remaining part of this *Third Notice* dealt with the transference of compounds that Hittorf had not examined in the *Second Notice*.

A paragraph in the *Fourth* and last *Notice*[45] worth noting comprised, beyond the determination of transference numbers, Hittorf´s critique of Clausius´ theory.[46] We will return to this theory below. Contrary to established opinion, Clausius postulated that free ions do exist in solution even in the absence of an electric potential due to their motion caused by their thermal energy. Hittorf strictly rejected this theory and commented on p. 584

> Der Schluß, zu den Hr. Clausius aus seinen Prämissen gelangt, steht meinen Erfahrungen nach mit der Wirklichkeit im Widerspruch, … Es sind bloß die letztgenannten Zersetzungen, welche die Theorie der Elektrolyse von Hrn. Clausius brauchen kann. Bis jetzt ist kein Chemiker so kühn gewesen, sie anzunehmen, … (The conclusion Mr. Clausius draws from his premises is, in my experience, at odds with reality, … Only the latter decompositions can use Mr. Clausius' theory of electrolysis. Until now, no chemist has been so bold as to accept it.)

We see that Hittorf was not only the target of criticism, but was himself a critic. The last part of this paper dealt with the determination and discussion of the transference of complex ions, and what he called "double salts".[19] Salts of cadmium and iodine, for example, which contain complex anions will play an important role in Arrhenius´ dissociation theory.

At the time of Hittorf publications transference numbers by his method were also determined by G. Wiedemann[47] and by A. Weiske.[48] These and Hittorf´s data were later used by Friedrich Kohlrausch in his studies of conductivities.

We already pointed out that a given ion has different transference numbers in electrolytes of different composition, depending on the counterion. For example, Hittorf determined $\tau_+$ of 0.63 for $Ag^+$ as acetate and of 0.47 as nitrate (ref. [36], p. 206).[20] From these data it follows that the silver ion velocity is 1.7 times higher than that of acetate, and about 10% lower than the nitrate velocity. Regrettably, the method provided only the relative ion velocities, but not the absolute values of the individual ion species. The decisive advance towards the solution of this problem was initiated by Kohlrausch's work on the conductivities of electrolyte solutions, in particular by his law of independent ion migration. We will discuss it below.

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[17] Svante Arrhenius, for example, was even lampooned when he presented his dissociation theory. Ironically, 25 years later he was awarded the Nobel Prize. We will tell this episode in the next Part 4 of our historical review series.

[18] Heinrich Gustav Magnus (1802, Berlin – 1870) was an influencing German chemist and physicist. In 1845 he became professor of physics, chemistry and technology at the University in Berlin. His students or coworkers were, among others, A. von Baeyer, E. Du Bois-Reymond, R. Clausius, P. von Groth, H. von Helmholtz, G. Kirchhoff, A. Kundt, E. Sarasin, J. Tyndall and E. Warburg.

[19] It can be assumed that the majority of readers have little interest in details. We have therefore included them in this footnote. These double salts consisted, for example, of *K*, *Ag*, and *CN*, or *Na*, *Pt*, and *Cl*. Their number was rather limited, since most were not stable when dissolved in water. Hittorf measured and discussed the transfer, for example, of the complex salts consisting of cadmium and iodine, which he was able to dissolve undecomposed in absolute ethanol and in amyl alcohol.

[20] These values are in good agreement with current transference numbers, at 25°C, e.g., of 0.624 for $Ag^+$ (0.01 mol.L$^{-1}$) as acetate and of 0.4648 as nitrate.[49]

The reader may wonder that this historical review does not even mention a certain empirical law which – as generally assumed – Friedrich Kohlrausch had confirmed by careful measurements in 1869.[50] It had, however, already been applied earlier, namely in the 1830s by Michael Faraday and in the 1850s by Wilhelm Hittorf in their investigations of the electrophoretic current in solutions of ions. It was also an indispensable law in further research on this subject and is still daily practice. What is meant is the law about the connection between electrical potential difference, resistance and current strength, which Georg Simon Ohm had found empirically in the middle of the 1820s, albeit for metallic wires, i.e., for 1st class conductors.[51-56] That it also applied to 2nd class conductors, that is to say, to solutions of ions, was by no means a foregone conclusion because of the fundamental difference in the nature of conduction. So how did it come about that Ohm's law proved to be valid also for solutions of ions?

## A LEAP IN TIME, BACK TO 1831: G. TH. FECHNER´S PROOF THAT OHM´S LAW APPLIES TO SOLUTIONS OF ELECTROLYTES

Before we get to Kohlrausch´s above-mentioned conductivity measurements, we have to realize that he did, in principle, measure the resistance or the specific resistance of the electrolyte solution, a property that we have yet not even addressed in this historical retrospect. To do this, we have to go back to the 1820s, to the time when Faraday made experiments in organic chemistry in Davy´s laboratory. At that time Georg Simon Ohm pioneered the research in electric resistance of 1st class conductors.

Ohm was not affiliated with the scientific community at the time of his research. He was a school teacher at the Jesuit Gymnasium in Cologne when he derived his law in mid-1820s. He performed his experiments in the laboratory of this college with wires made of different metals and various lengths and diameters. He published his preliminary results initially in two treatises in 1825.[51, 52] As he was not satisfied with his work,[21] he developed a new theoretical approach, which led to the law named after him. This well-known law says that the current strength is directly proportional to the electric potential difference and indirectly proportional to the resistance of the conductor. Ohm published his new theory in 1826.[53-55] In his *opus magnum* "*Die galvanische Kette, mathematisch bearbeitet*" (*The galvanic chain, mathematically processed*) [56] he summarized in 1827 the results together with a comprehensive mathematical treatment.

Ohm´s work did not attract much attention, but the interest changed when French physicists claimed priority of the law for Claude Servais Mathias Pouillet,[22] who rediscovered Ohm´s law years later and published his results in 1837[57] (German version in ref. [58]; the editor, Johann Christian Poggendorff, added a critical comment to this version, cited in footnote [23]). Pouillet derived the according relations rather from experimental results which was considered as being superior to Ohm´s merely theoretical approach.

His assertion of priority provoked a heated debate, led primarily by Jean Claude Eugène Péclet, who published a harsh rebuff of Pouillet's claim in an essay entitled "*Lettre touchant un passage de la dernière édition du Traité de Physique de M. Pouillet*" (*Letter concerning a passage in the last edition of the Traité de Physique by M. Pouillet*)[61] stating

> C'est seulement en 1837 que M. Pouillet a publié son Mémoire dont toutes les formules se déduisent de celles de M. Ohm par de simples transformations, comme M. Henrici l'a démontré (Annales de Poggendorff tomes LIII[62] et LIV[63] ), … (It was not until 1837 that M. Pouillet published his Memoir, all the formulas of which can be deduced from those of M. Ohm by simple transformations, as M. Henrici has shown (Pogg. Annal. LIII and LIV),…)[24]

Finally and at last Ohm's priority was recognized internationally, and in 1841 he received the prestigious Copley Medal from the Royal Society in London. Nevertheless, in Germany it lasted until 1852 that he became professor for experimental physics at the University in Munich, at the age of 63, two years before his death.

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[21] In the last two sentences at the end of his second paper from 1925,[51] Ohm complained about the lack of support for his research: "*Meine Arbeit·fängt allmählig an, sich zu einem Ganzen zu runden. Nur bedaure ich, daß ich häufig aus Mangel an Mitteln, Untersuchungen abbrechen muß, die ich so gern weiter verfolgt hätte*" (*My work gradually begins to round off into a whole. My only regret is that I often have to abandon investigations that I would have liked to pursue further, due to lack of funds.*)

[22] We quoted Pouillet already in the Introduction of this review.

[23] Poggendorf commented: „*Wiewohl die Resultate dieser Abhandlung zum Theil nur Bestätigungen der von Ohm („Die GaIvanisehe Kette" und Schweigg. Journ. Bd. XXXXVI S. 137),*[59] *entdeckten, auch von Fechner (Maaßbestimmung über die galvanische Kette) und früher von Pouillet selbst (Annal. Bd. XV S. 91)*[60] *beobachteten Gesetze sind, so schien doch die unverkürzte Mittheilung derselben,schon weil sie so wenig berücksichtigt wurde sind, nicht überflüssig. P.*" (*Although the results of this treatise are partly only confirmations of the laws discovered by Ohm ("Die GaIvanisehe Kette" and Schweigg. Journ. Bd. XXXXVI p. 137),*[59] *also by Fechner (Maaßbestimmung über die galvanische Kette) and earlier by Pouillet himself (Annal. Bd. XV p. 91)*[60] *so the unabridged communication of them seemed not superfluous, already because they were so little considered. P.*) [citations added by the author].

[24] Complete literature sources added by the author.

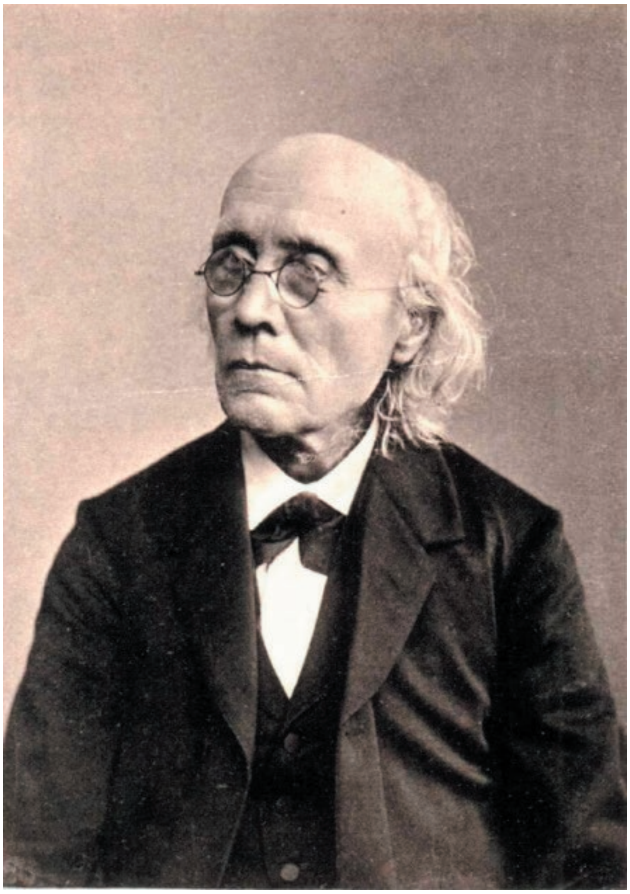

**Figure 3.** Portrait of Gustav Theodor Fechner (1801 – 1887). Date and author unknown. Source, ref. [64], public domain.

Initially regarded of minor importance, his law was later recognized as highly significant for the technology of ever-widening electrical telegraphy, especially after the mid-1850s with the introduction of the single-wire system by Samuel Morse.

We have mentioned above that after his publication in 1827 Ohm´s work was widely ignored, and only few scientists recognized its importance, with Gustav Theodor Fechner[25] as Ohm´s main supporter (his portrait is shown in Figure 3).

Fechner's scientific merits should not be underestimated, although they were, because he extended Ohm's theory of the 1st to 2nd class conductors. His work is therefore indispensable for electrophoresis. He is also worth noting because, in addition to his scientific interests, he had a penchant for writing satirical pseudo-scientific works. In 1821 he published his first paper ever; it was entitled "*Beweis, daß der Mond aus Jodine bestehe*" (*Proof that the moon consists of iodine*),[65] published under his pseudonym Dr. Mises. It is a humorous pamphlet against materialistic medicine. Of similar kind was his scientific satire from 1825 "*Vergleichende Anatomie der Engel*" (*Comparative anatomy of angels*).[66]

In these early 1820s, Fechner prepared the translation of Jean-Baptiste Biot´s textbook "*Précis élémentaire de physique expérimentale*"[67, 68] into German, which appeared in 1824 and 1825, but he found the description of electricity and of the theory of galvanism in this book highly out of date. In order to raise these themes to the contemporary level, he decided to upgrade it by Ohm´s theory. At this occasion, he found keen interest in this topic, and expanded his research from the hitherto investigated metallic conductors to liquids, pioneering in this way the quantitative context of electric potential difference, current and resistance in ion solutions.[26] After two years of extensive experimental work, Fechner presented his results and conclusions in the book "*Massbestimmungen über die galvanische Kette*" published in 1831.[69]

Fechner demonstrated that Ohm´s law not only applies to metallic conductors, but also to electrolyte solutions. He gave a résumé of these findings (amongst others) by stating on pp. 235-236 of his book

> … (i) Der Leitungswiderstand der Flüssigkeiten ist dem Abstande der Erregerplatten darin direct proportional… (ii) Der Widerstand der Flüssigkeit steht im umgekehrten Verhältnisse des Querschnittes der Flüssigkeit… .(iii) Der Widerstand der Flüssigkeit ist unabhängig von Beschaffenheit der Plattenpaare… (iv) Der Widerstand der Flüssigkeit nimmt ab mit der Quantität saurer oder salziger Bestandtheile, die man in dieselbe hinzufügt. (v) Durch fortgehends gleiche Zumischungen gleicher Antheile Säure wird der Widerstand des Brunnenwassers auch fortgehend um gleiche Quantitäten verringert…" ((i) The electric resistance of the liquids is directly proportional to the distance of the excitation plates therein. (ii) The resistance of the liquid is in inverse proportion to the cross section of the liquid … (iii) The resistance of the liquid is independent of the nature of the plate pairs … (iv) The resist-

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[25] Gustav Theodor Fechner (1801, Groß-Särchen, now Żarki Wielkie, near Muskau in Lower Lusitia – 1887, Leipzig) attended the Academy of Arts in Dresden from 1814, and studied medicine there from 1817 and in Leipzig from 1818, where he graduated in 1823. However, he left the field of medicine and completed his habilitation in 1823 at the Philosophical Faculty. He was appointed professor of physics in 1834; his research focused on galvanism and optics. Due to a severe eye complaint from 1840 to 1843, he retired. In 1860 he expanded Weber´s law to Weber-Fechner law. This law expresses the non-linear relationship between psychological sensation, $S$, and the physical intensity, $I$, as $S = K \ln I$.

[26] The water Fechner used in his experiments can be considered rather as a dilute electrolyte solution. Water with the highest purity which was available for him was well water, which certainly contained a relatively high amount of ions. All the more his results are to be appreciated.

> ance of the liquid decreases with the quantity of acidic or salty components are added to it. (v) By continuously adding equal amounts of acid, the resistance of the well water is also continuously reduced by equal quantities…)

If we convert these formulations into a modern notation, we get for a given solution that (i) $R=prop\ l$; (ii) $R=prop(1\text{-}A)$; (iii) $R\neq f(\mathrm{U})$; (iv) and (v) $R=prop(-S.c)$. Symbol $R$ stands for the electrical resistance of the liquid, $l$ is the distance between the electrodes, $A$ is the cross sectional area of the electrodes, $U$ is the electrical potential difference, and $c$ is the concentration of acidic or salty additives to water; $S$ is a factor of proportionality. It is seen that these findings actually represent the first evidence that Ohm´s law also applies to liquid conductors.[27] It is worth noting that the combination of (i) and (ii) leads to equation $R=prop(l/A)$, in accordance with modern notation as $R=\rho l/A$, in which $\rho$ is termed electrical resistivity or specific electrical resistance.

After his retirement, Fechner focused mainly on philosophy and topics of psychophysics and psychological aesthetics. During this time he published works mainly based on *Natur Philosophie* and religious-mystical ideas.[28]

## R. CLAUSIUS' THEORY: FREE IONS ARE PRESENT IN ELECTROLYTE SOLUTIONS EVEN WITHOUT AN APPLIED ELECTRIC FIELD

Coming back now from Fechner´s time to 1852, when Rudolf Clausius[29] turned his interest on 2nd class conductors after publishing his paper about the work done on 1st class conductors and the heat generated thereby[30],[84-86] In "*Ueber die Elektricitätsleitung in Elektrolyten*" from 1857[46] (Engl. vers., *On the Work performed and the Heat generated in a Conductor by a Stationary Electric Current*,[87] French vers., *Mémoire sur la Chaleur dégagée par les courants électriques.*[88]), Clausius expressed his rejection of the established view of the transport of electric charges through electrolyte solutions, a theory that was going back to Theodor von Grotthuß. Even in Clausius´ time (and later), it was generally assumed that the electrolyte molecules, called the *complete molecules* by him, were composed of atoms or groups of several atoms, which he called *partial molecules.*[31] Each molecule consists, as was believed, of two tightly bound partial molecules of opposite charge (i.e., ion and counterion). We recall that in the theories of Grotthuß and Davy the molecules form a continuous chain that extends without gaps from one electrode to the other. Only the terminal molecules of this chain are in direct contact with the electrodes and are the first to be decomposed during electrolysis. Then, an instantaneous recombination of the ions with the counterions of the neighboring molecules, and the decomposition of the newly formed molecules happens along the entire chain. We will not repeat this mechanism of the flow of electricity as we discussed it in detail in the previous Part 2 of our series.[4] Important to emphasize is that the established theories of Grotthuß and Davy exclude the presence of free ions in solution in the absence of an electric potential, because an electric force would be mandatory to separate the tightly bound ions of a molecule.

In his said paper from 1857 Clausius radically broke with this conventional view[46, 87, 88] He first considered a liquid that contains "electrolytic molecules", i.e., electrolytes. Clausius' basic condition for all further considerations was that electric neutrality had to be in every volume element of the liquid. If there was no external electric force, the molecules were dispersed in an arbitrary order and possibly vibrated around a certain equilibrium position. He further assumed that in the same molecule the attraction between ion and counterion, which are close to each other, is greater than the attraction of one ion to the counterion of another molecule.

Clausius assumed, in analogy to his paper "*Ueber die Art der Bewegung, welche wir Wärme nennen*"[90] (*The nature of the motion which we call heat*)[91] from

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[27] It is clear that points (iv) and (v) do not have counterparts in pure metals, but the observations were nevertheless correct and preceded at least within a small concentration range the measurements of the conductivities by F. Kohlrausch.

[28] Fechner published, for example, poems,[70] a book about *the soul life of plants*,[71] 3 vol. about *things of heaven and the hereafter*,[72][73][74] about psychophysics,[75][76][77][78] a book with the mysterious title *"the day view versus the night view"*,[79] but also a paper in Pogg. Ann. Phys. Chem. "*Ueber die Bestimmung des wahrscheinlichen Fehlers eines Beobachtungsmittels durch die Summe der einfachen Abweichungen*" (*On the determination of the probable error of an observation mean by the sum of the simple deviations.*)[80]

[29] Rudolf (Julius Emanuel) Clausius (1822, Köslin, province of Pomerania in Prussia, now Koszalin, Poland) -1888, Bonn] is one of the first theoretical physicist of the Nineteenth century and a central founder of thermodynamics (2nd law of thermodynamics), and the kinetic gas theory. He created the concept of entropy and contributed significantly to fundamental concepts of statistical mechanics. Less known is his work on free ions in solutions, which he carried out mainly during his research activities as professor at the ETH in Zürich in the 1850s.

[30] In this paper Clausius derived the theoretical basis of the empirical results of J. P. Joule,[81] M. E. Lenz, the father of Robert Lenz[82] and Edmond Becquerel.[83]

[31] Clausius did not use the terms ion, anion and cation in this paper, although they have been known since 1834, when Michael Faraday introduced them.[89] Clausius differentiated the neutral "*Gesamtmolecüle*" (*complete molecules*), which were combinations of the oppositely charged ions, which he called "*Theilmolecüle*" (*partial molecules*). For the sake of simplicity, we name Clausius´ "*complete molecule*" as molecule, and, "*partial molecules*" as ions, and cations and anions if appropriate.

the same year that – in absence of an electric field – the electrolyte molecules do not remain permanently in the liquid in an equilibrium position around which they oscillate. On the contrary, they are moving and their motion is irregular. Moreover, an ion can be disconnected from its molecule due to its thermal energy and then moves randomly between the other molecules in the solution. It can happen that this ion attracts the counterion of another molecule more strongly than the ion and counterion of this molecule attract themselves. In this case, this ion and the counterion of the molecule form a new molecule and the parent ion is set free. It then moves in the solution between the other molecules and reacts with one of them in the manner just described; then the whole process continues.

A second possibility for the formation of free ions assumed by Clausius was that two different molecules interact with each other. In this case, it can happen that the ion of one molecule takes a preferred position over the counterion of the other molecule and these two ions combine to form a new molecule. This process releases two ions, which either combine to form a new molecule or disperse between the other molecules in the solution and act there as described above. We emphasize again that we have described the situation in the absence of an external electric force. It was considered by Clausius as the natural state of electrolytes in solution.

When an external electrical force acts, the first reaction of the molecules would be to rotate into the proper position towards their respective electrodes (what Davy and Berzelius did not take into account, but Hittorf did). Then the force would separate ion and counterion of a molecule and drive them in opposite directions. In this case the ion of one molecule may combine with the counterion of the other. However, this can only happen if the attractive force between the ion and the counterion of the one molecule is overcome. Clausius argued that the influence of the external electric force not only starts from a certain strength, but that even the slightest force acts in the manner described above. The magnitude of the effect increases with the strength of the force. That is, the effect fully complies with Ohm's law. He wrote (we reproduce verbatim the Engl. version, ref. [87], p. 99-100)

> But in order to separate the already combined partial molecules, the attraction which they exert upon each other must be overcome, for which a force of a certain intensity is necessary; hence we are led to the conclusion, that so long as the force acting within the conductor does not possess this requisite intensity, no decomposition whatever can take place; but that, on the other hand, as soon as the force has attained this intensity, a great many molecules must be simultaneously decomposed, inasmuch as all are exposed to the influence of the same force, and have almost the same relative positions to each other.

and continued

> So long as the moving force acting within the conductor is below a certain limit, it causes no current whatever; so soon as it attains this limit, however, a very strong current is suddenly produced. *This conclusion, however, is in direct contradiction to experiment.* The smallest possible force gives rise to a current accompanied by alternate decompositions and recombinations, and the intensity of this current increases in proportion to the force, according to Ohm's law.

However, in the original paper written in German, this passage has another meaning; it reads (ref. [46], p. 346-347)

> So lange die im Leiter wirksame treibende Kraft unter einer gewissen Gränze ist, bewirkt sie gar keinen Srom, wenn sie aber diese Gränze erreicht hat, so entsteht plötzlich ein sehr starker Strom. *Dieser Schluß widerspricht aber der Erfahrung vollkommen*. Schon die geringste Kraft bewirkt einen durch abwechselnde Zersetzungen und Wiederverbindungen geleiteten Strom, und die Intensität dieses Stromes wächst nach dem Ohm'schen Gesetze der Kraft proportional. [The reader's attention is drawn to footnote [32]].

If an external electric force acts, the cations and the anions in the solution do not move randomly, but are driven in opposite directions. In addition, the force facilitates the decomposition of the molecules, and the detachment of an ion from its molecule occurs more frequently than without such electric force. Clausius assumed that the number of positive and negative ions which move in opposite direction is not necessarily equal, it depends on their activity of molecular motion, which can be different for different ions. The counter-directed movement of both types of ions represents the galvanic current[33] in the liquid. Its strength is given by the sum of the flows of both ions.

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[32] The author would like to add a note here. He refers to the misleading or even wrong translation of Clausius' original work in the English version, which he has marked in italics in the main text. Clausius wrote verbatim: "*Dieser Schluß widerspricht aber der Erfahrung vollkommen*." The English version reads: "*This conclusion, however, is in direct contradiction to experiment*." The term *Erfahrung* is translated here by *experiment*, but the correct translation is *experience* – in fact a crucial difference. In the French version the sentence is correctly translated as *"… En d´autres termes, aussi longtemps que la force est au-dessous d´une certaine limite, il n´y a pas de courant, et dès que cette limite est dépassée, il nait subitement un courant intense. Cette conclusion est évidement contraire à l´expèrience."*, ref. [88], p. 254.)

[33] We call it, as defined in the previous parts of our review, the electrophoretic current. It is not the flow of charges carried by electrons. The

This theory also offers the explanation why the conductivity of a 2nd class conductor increases with increasing temperature: it is because the greater the activity of motion of the particles due to their thermal energy in the solution, the more the decomposition of the molecules is facilitated.

Although Clausius' innovative theory of the permanent presence of free ions offered new explanations for the properties of electrolyte solutions and became widely known, it is noteworthy that the majority of the scientific community (but not its elite) did not replace the theory published by Grotthuß half a century ago in 1805. This lack of scientific acceptance was criticized, to quote an arbitrarily chosen example, in an 1879 publication, another two decades after Clausius' work. Franz Exner,[34] professor of physics at the University of Vienna and teacher of two Nobel Laureates, pointed out in his publication "*Ueber die Electrolyse des Wassers*" (*On the electrolysis of water*), ref. [92], p. 350)

> … dass die Clausius'sche Hypothese über die Constitution der Flüssigkeiten der Theorie der Electrolyse… mit den bekannten Thatsachen nicht nur nicht im Widerspruche steht, sondern durch dieselben auf das Entschiedenste bestätigt wird. Unter allen Umständen aber ist es an der Zeit, die jetzt noch fast ausschliesslich citirte Grotthuss'sche Theorie der Electrolyse endgültig fallen zu lassen; denn seit wir … einen klarern Einblick in das Wesen dieser Vorgänge erlangt haben, erscheinen die von der Grotthuss'schen Theorie geforderten, von Molecül zu Molecül fortschreitenden Zersetzungen und Wiedervereinigungen als eine absurde Vorstellung. (… that Clausius' hypothesis of the constitution of liquids does not contradict the theory of electrolysis … not only with the known facts, but is most decidedly confirmed by them. Under all circumstances, however, it is high time to finally abandon Grotthuß´ theory of electrolysis, which is almost exclusively cited; for since we … have gained a clearer insight into the nature of these processes, the decompositions and reunifications which progresses from molecule to molecule, as required by Grotthuß´ theory, appear to be an absurd notion.)

It took nevertheless another decade before the existence of free, non-associated ions, as formulated in Svante Arrhenius´ seminal theory, was accepted, albeit reluctantly and against fierce opposition.

## F. KOHLRAUSCH'S FUNDAMENTAL CONTRIBUTIONS TO ION CONDUCTIVITY, VELOCITY AND MOBILITY

Friedrich Kohlrausch,[35] who coined the subject of ion conductivity and ion migration (of strong electrolytes) in the next decades, concluded his habilitation in 1863, not in electrochemistry, but "*Ueber die elastische Nachwirkung bei der Torsion*"[93, 94] *(Elastic aftereffects during torsion*) at the University of Göttingen, where he became private docent in 1866 and in 1867 associate professor. During the four years in Göttingen from 1866 to 1870 he was mainly, though not exclusively, engaged in research on geomagnetic and electrical measurements, and in investigations of the resistance and conductivity of electrolyte solutions.[36]

### *Kohlrausch's Entry into Electrochemical Research in 1868*

Together with his coworker and former doctoral student Wilhelm August Nippoldt[37] Kohlrausch published his first contributions to electrochemistry in 1868 and 1869 in various versions.[50, 105-107] The overarching subject of these papers was "*Ueber die Gültigkeit der Ohmschen Gesetze für Elektrolyte und eine numerische Bestimmung des Leitungswiderstandes der verdünnten Schwefelsäure durch alternierende Ströme*" (*On the validity of Ohm's laws for electrolytes and a numerical determination of the electric resistance of dilute sulfuric acid by alternating* currents).[106, 107] In this paper, Kohlrausch and Nippoldt posed three questions: (1) How can the influence of the polarization of electrodes be exclud-

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charges are carried – notabene – by ions, which is the unique feature of electrophoresis.

[34] Franz Serafin Exner (1849, Vienna – 1926) was an Austrian physicist. In 1891 he became professor of physics at the University of Vienna and succeeded J. J. Loschmidt. His best-known students were the Polish physicist Marian Smoluchowski, and the Austrian physicists Erwin Schrödinger (Nobel Laureate for physics 1933), and Victor Franz Hess (Nobel Laureate for physics 1936).

[35] Friedrich Kohlrausch (1840, Rinteln-on-Weser – 1910) was a German physisist. He studied physics in Erlangen and Göttingen, where he received his doctoral degree in 1863. In 1867 he was appointed to a professorship in Göttingen. Famous for his exact experimental work, his accurate measurements and his outstanding level in research, Kohlrausch became professor at ETH Zurich in 1870, at Technical University Darmstadt in 1871, at the University of Würzburg 1875, and at the University of Strasbourg as from 1888. He was successor of H. von Helmholtz at the Physikalisch-Technischen Reichsanstalt in Berlin, where he was director between 1895 and 1905. The Reichsanstalt was founded in 1887 and was the first government-financed research institution worldwide, where their staff members – in contrast to the Universities – were not committed to teach. Prominent members were Walther (Hermann) Nernst (1864 – 1941), Emil (Gabriel) Warburg (1846 – 1931), Walther (Wilhelm Georg) Bothe (1891 – 1957), Albert Einstein (1879 – 1955) and Max (Karl Ernst Ludwig) Planck (1858 – 1947).

[36] Beside these main topics he also dealt, e.g., with the construction of an apparatus which serves for room cooling,[95]. the speed of propagation of the stimulus in the human nerves,[96] elastic effects after torsion,[97][98] geomagnetic observations in Göttingen,[99][100][101][102] the amount of electricity generated by an influence machine,[103] and others.

[37] The title of Nippoldt´s dissertation was "*Untersuchungen über den galvanischen Widerstand der Schwefelsäure bei verschiedenen Konzentrationsgraden*" (*Studies on the galvanic resistance of sulfuric acid at various degrees of concentration.*)[104]

ed when determining the electrical resistance of liquids? (2) Does Ohm's law also apply to decomposable conductors?[38] And connected with this: How can Clausius' postulate be proven that Ohm's law still holds for the smallest possible electromotive forces? (3) How does the electrical resistance of decomposable conductors depend on their concentration?[39]

Clausius explicitly pointed out in his paper about free ions from 1858, discussed above, that "*The smallest possible force gives rise to a current accompanied by alternate decompositions and recombinations, and the intensity of this current increases in proportion to the force, according to Ohm's law.*" Since Clausius gave no experimental results for this "smallest possible force", and did not cite any sources in which this force was given,[40] we find this central argument vague and indefinite and a weak point in Clausius' chain of reasoning (see also footnote [32]).

However, Kohlrausch and Nippoldt took up this challenge and attempted to measure a critical value of this force. Unable to achieve a sufficiently low alternating current, they applied thermoelectric current instead, generated by a pair of Cu-Fe wires. And indeed, Kohlrausch and Nippoldt were able to spectacularly determine the lowest electromotive force at which the electrolytic decomposition of the zinc vitriol solution still occurred, i.e., they measured whether or not current and emf were in direct proportion.[41] Their results led them to conclude that *"... die Gültigkeit des Ohmschen Gesetzes ... bis zu einer elektromotorischen Kraft von 0,00000233 oder 1/429000 Grove hierdurch als bewiesen ansehen kann*" (*... the validity of Ohm's law ... down to an electromotive force of 0.00000233 or 1/429000 Grove can thus be regarded as proven*). This emf in Grove is equivalent to $4{,}2.10^{-6}$ V. Referring to the work of H. Buff from 1855,[110] Kohlrausch and Nippoldt deduced that this weak electrical force which decomposed their electrolyte was greater than the force of its chemical affinity. Thus they agreed with Clausius' theory, but their conclusion was based on factual data (p. 379). They ended the paper with the nonetheless qualifying remark

> Die Prüfung des Ohmschen Gesetzes für Elektrolyte auf noch kleinere Kräfte als die obigen auszudehnen, darf weder als überflüssig noch als unmöglich bezeichnet werden. (To extend the test of Ohm's law for electrolytes to even smaller forces than the above may be said to be neither superfluous nor impossible.)

The first and third questions posed above related to one of the main sources of errors in measuring the electrical resistance and conductivity of liquids, namely the polarization of the electrodes. Two options were known to minimize polarization. To use alternating instead of direct current; and to measure with amalgamated zinc electrodes, that were not polarized. Kohlrausch and Nippoldt opted for alternating current, which they generated in their laboratory using a rather elaborate device they built themselves.[42] They mounted, in addition, large-area platinum electrodes to reduce the current density there.

Sulfuric acid as the test substance was diluted in water at different percentages[106, 107] and the resistances were determined.[43] Their reciprocals, the "relative conductivities", are plotted in Figure 4. They were in accordance with earlier contributions by other authors, but were more accurate.

The curve of the relative conductivity of the solution vs. the specific weight of the sulfuric acid diluted in steps of ten (percentage of acid) increased at low concentrations, but then reached a maximum at 1.233 specific weight which equals 31.5 weight % of sulphuric acid hydrate (the "hydrate theory" is addressed in the following Part 4 of our historical reviews).

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[38] Kohlrausch and Nippoldt called here electrolyte solutions, i.e., 2nd class conductors, as opposed to metals, "decomposable conductors".

[39] Kohlrausch, of course, was not the first to research the conductivity or resistance of electrolyte solutions. Such earlier investigations had been discussed and compared in G. Wiedemann`s "Galvanismus"(ref. [108], pp. 191-208). Wiedemann reported on A. de la Rive (1830); G. T. Fechner (1831), see the Chapter "Leap in Time" above; C. S. M. Pouillet (1837); M. E. Lenz (1838); F. C. Henrici (1845) W. G. Hankel (1846); E. Becquerel (1846); E. N. Horsford (1847); E. Becker (1850, 1851); G. Wiedemann (1856); A. Saweljew (1856); W. Schmidt (1859). None of these researchers, however, has systematically studied this topic for about four decades and none of them has contributed with such fundamental findings. In this respect, the justification that Kohlrausch has coined the topic seems appropriate.

[40] In a letter to the Chairman of the Deutschen Bunsengesellschaft, W. Nernst, from May 24, 1908, Kohlrausch himself wrote about Clausius' argumentation and his and Nippolt´s measurement: "*Nach den von Clausius entwickelten Vorstellungen dürfte dies wohl als wahrscheinlich gelten, war jedoch niemals an der Erfahrung gepriüft worden. Diese Lücke wurde ausgefüllt.*" (*According to the ideas developed by Clausius, this is very likely, but had never been tested on experience. This gap was filled.*).[109], p. 385. Note that Kohlrausch insisted on a test.

[41] The solution of zinc vitriol (i.e., zinc sulphate) electrolyzed by amalgamated zinc electrodes to exclude polarization contained 16.6 g of the salt in 100 g solution. This solution was filled into a tube with 2400 $mm^2$ cross-sectional area and had a length of 83 mm. The current was measured with Nobili's astatic galvanometer.

[42] In their first electrochemical experiments, Kohlrausch and Nippoldt used a rather complicated apparatus to generate alternating current, which was later replaced by one that was much easier to handle. They produced equal but oppositely directed currents of short duration and rapid succession by induction with a rotating magnet using large-area platinum electrodes (later, a small induction coil was used). The number of revolutions of the magnet was determined by means of a siren fixed in the axis of the magnet and its pitch was compared with a set of organ pipes. The induction currents were observed with a sensitive Weber bifilar dynamometer, which was later replaced by a Wheatstone bridge.

[43] The resistance was related to that of mercury.

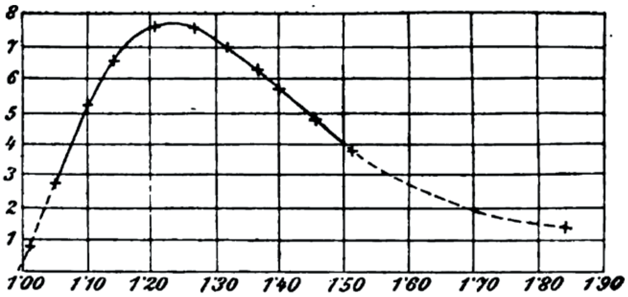

**Figure 4.** "Relative Leitfähigkeit" (relative conductivity) vs. specific weight (also density) of dilute sulphuric acid. The resistance was measured with alternating current as described in the main text. Abscissa: specific weights of the acid solution at 18.5°C from 1.0504 to 1.5025, corresponding to a content of the acid from 8.3 to 60.3%. The curve depicts the "Leitungsvermögen" at 22°C. From ref. [107], p. 386.

Kohlrausch´s finding that the conductivity depends on the concentration of the dissolved electrolyte initiated one of his major research activities. He carried out analogue measurements, also with alternating current,[44] and published the results in 1875 with Otto Grotrian,[111, 112] and in 1876 in a paper with a similar content, but with an improved experimental set-up.[113] In the same year he published the preliminary version of the *law of independent ion migration*,[114] the subject of the following chapter.

## *The Law of Independent Ion Migration: 1st Kohlrausch Law*

Around the 1850s several authors, to name Wilhelm Hankel,[115] Gustav Wiedemann[39, 47] and Wilhelm Beetz[116] investigated the relationship between the electrical resistance of electrolyte solutions and their viscosity.[45] In 1856 Wiedemann came to the preliminary conclusion that under the conditions of his experiments (ref. [47], p.229) " *… würde … der Leitungswiderstand der Zähigkeit der Flüssigkeiten direct … proportional seyn***.** *(…would … the resistivity be directly proportional to the viscosity of the liquids***.**)[46]

The German physicist Georg Quincke[47] modeled in 1871 the resistance to the motion of "*Theilmolecüle*" (*partial molecules*), the ionic constituents of a "*Gesammtmolecül*" (*complete molecule*) in a thin thread of a liquid solution and brought into play not only the viscosity of the liquid but also the mutual attraction and repulsion of the ions.[123] He argued that this electrical interaction is compensated by the corresponding effect of the neighboring counterion and is therefore irrelevant, and concluded that

> Die specifisches Leitungsfähigkeit der gesamten Flüssigkeit ist gleich der Summe der partiellen specifischen Leitungsfähigkeiten der einzelnen Bestandtheile. (The specific conductivity of the entire liquid is equal to the sum of the partial specific conductivities of the individual components.)

This reads in eq. (26) on p. 16 that $\lambda = \lambda_1 + \lambda_2 + \ldots \lambda_r$. Here, $\lambda$ is the specific conductivity of the solution, and $\lambda_i$ are those of the individual ionic constituents, the *partial molecules*, with *i* ranging from 1 to *r*.[48]

In the second half of the 1870s Otto Grotrian found a striking connection between electric resistance and mechanic frictional resistance.[124, 125] Rudolf von Lenz, in the same years, investigated a relationship between the resistance of haloïd salt solutions and their density (not of their viscosity).[126, 127] All researches agreed that the liquid of the solution decelerates the motion of the ions and thus increases the resistance of the current. By the way, this is a prerequisite for a constant migration velocity of an ion driven by a constant force in the theory of electric lines of action of Michael Faraday (see Part 2, Chapter 3.1.6.).

This point of view was shared by Kohlrausch, who supposed that the source of the frictional resistance and thus the influence on the migration velocity of the ions in dilute aqueous solutions can only come from the water molecules due to their large excess over all other constituents. Taking into account this connection between electrical force and mechanical resistance in ion transport, Kohlrausch came up with the key idea that

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[44] The salt content in the solutions was between ca. 3% and 30% (w/w). It seems perhaps superfluous to nearly always indicate the concentrations of the electrolytes in the respective measurements. However, this is not the case, since they play a central role in the migration properties of the ions.

[45] The device to measure the viscosity was based on the findings of the German hydraulics construction engineer Gotthilf Ludwig Hagen[117] and the French physiologist and physicist Jean Léonard Marie Poiseuille.[118][119][120] The device resembled the nowadays used standard U-tube viscometer.

[46] See also refs. [39], pp. 169, 170; [108], pp. 421-426; [121], pp. 632-634, and [122]

[47] Georg Hermann Quincke (1834, Frankfurt/Oder – 1924, Heidelberg) studied physics, chemistry and mathematics, and presented his doctoral thesis on "*Kapillarerscheinungen bei Quecksilber*" (*Capillary phenomena with mercury*) at the Humboldt-University in Berlin in1858. In 1875 he became successor of Gustav Kirchhoff at the University of Heidelberg, where he retired in 1907. Interesting for the present subject are his scientific activities in capillarity, in the electric properties of colloidal particles and in electroosmosis (we will come back to these important contributions in a later review).

[48] Note that Quincke used Clausius´ phraseology, and that this equation has some similarity with Kohlrausch´s law of independent ion migration.

the extent of this mutual influence is most likely different for different ions, which would lead to their unequal migration velocities. He communicated his hypothesis in 1876 – the preliminary version of the law of independent ion migration – and confidently stated (ref. [114], p. 215)[49]

> Ist nun die Lösung sehr verdünnt, so wird diese Reibung vorwiegend an den Wassertheilchen stattfinden. Demnach wird man weiter zu schließen versucht sein – *und dies ist ein Schluß, der meines Wissens noch nicht gezogen worden ist* – daß jedem elektrochemischen Elemente (z. B. dem Wasserstoff, Chlor oder auch einem Radicale wie $NO_3$) als solchem ein bestimmter Widerstand in verdünnter wässeriger Lösung zukommt, gleichgültig, aus welcher Verbindung es elektrolysirt wird. (If the solution is very dilute, this friction will mainly take place on the water particles. Accordingly, one will be tempted to conclude further – *and this is a conclusion which, to my knowledge, has not yet been drawn* – that every electrochemical element (e.g., hydrogen, chlorine or even a radical like $NO_3$) as such has a certain resistance in dilute aqueous solution, regardless of the compound from which it is electrolyzed.)

He argued, on the one hand, that the current is related to the sum of the velocities ($v_-+v_+$) of the two oppositely charged ions.[50] The current is, according to Ohm's law, also in inverse proportion to the resistance, that is to say, it is proportional to conductivity $\Lambda$. Hence the conductivity is proportional to ($v_-+v_+$).[51] He pointed out that, on the other hand, Hittorf´s transference number expresses the ratio of the velocity of an ion to the sum of the velocities of both ions, e.g., for the anion by $\tau_-=v_-/(v_-+v_+)$. For two electrochemically equal electrolytes, (1) and (2), with a common anion and with cation velocities of $v_+^{(1)}$ and $v_+^{(2)}$, respectively, he set $\Lambda^{(1)}/\Lambda^{(2)}=(v_-+v_+)(v_-^{(1)}+v_+^{(2)})$, expanded the equation by $v_-$, and obtained the relationship $\Lambda^{(1)}/\Lambda^{(2)}=\tau_-^{(2)}/\tau_-^{(1)}$. The corroboration of his hypothesis required that the ratio of the conductivities of the solutions of two electrolytes with a common ion had to be equal to the inverse ratio of the transference numbers of the common ion (it was already noted above that the transference number of an ion in an electrolyte depends on its counterion).

Kohlrausch scrutinized his hypothesis on the basis of transference numbers of about a dozen electrolytes from monobasic acids[52] (salts of alkalis and earth alkalis as chlorides, bromides, iodides, nitrates, perchlorates and acetates), and actually found a good agreement with his theoretical prediction. Thus he concluded on p. 219

> Die Annahme von der unabhängigen Beweglichkeit der Ionen läßt sich zweitens durch die Überführungszahlen allein prüfen und hierdurch auch an Körpern, deren Leitungsvermögen noch nicht bekannt ist, bestätigen oder widerlegen. (Secondly, the assumption of the independent migration of the ions can be proved by the transfer numbers alone and thus confirmed or disproved on bodies whose conductivity is not yet known.)

To this end, Kohlrausch took four compounds, which were composed of two pairs of ions, and related their resulting eight transference numbers to one another. In fact, he was able to calculate “Beweglichkeiten” (verbatim “mobilities”), the velocities relative to that of hydrogen. This hypothesis must not be confused with the final *law of independent ion migration* Kohlrausch published three years later.[130]

At the end of his 1876 paper (on p. 222) he came nevertheless to the conclusion that further experimental investigations were necessary to decide whether this aforementioned statement applies also in general or not. He began to examine systematically and with exceptional accuracy numerous aspects of the influence of various

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[49] In this early paper he took values for electrolyte concentrations in the low weight percent range.

[50] In the following discussion electrolytes with two single-charged ions are considered for the sake of simplicity (for other electrolytes the corresponding equations have to be extended by the numbers of ions, v, and the charge numbers, z. Since electrolytes with $v_-=v_+$ and $z_+=|z_-|=1$ are regarded, the molar and the equivalent concentrations and the respective conductivities are the same.

[51] We point out that at the time of Kohlrausch there was no standardized terminology, nor were the symbols of the physical and chemical quantities unified. Kohlrausch, for example, used the terms_“Leitungsvermögen” or “Leitfähigkeit” of the solution, which is “conductibility” or “conductivity” in English, and ascribed it in some papers by symbol $k$, in others by $\Lambda$. More misleading is Kohlrausch´s usage of the term “Beweglichkeit”, with symbols $l_+$ and $l_-$, in other papers $u$ and $v$, which is translated into English as “*mobility*” (a point that has been mentioned in the English translation of Kohlrausch´s paper from 1876[114] in Harper's Scientific Memoirs from 1899 (ref. [128], footnote at p. 89). In Kohlrausch's paper from 1876 “Beweglichkeit” is a dimensionless number, which is the velocity of migration of an ion related to that of hydrogen. The latter has the arbitrarily chosen value of 1. Kohlrausch initially formulated in his hypothesis of independent ion migration that the conductivity is the sum of the “Beweglichkeiten” of the ions, which he expressed by $\Lambda=(l_++l_-)$ or by $k=(u+v)$ (comp. with the different notations given in the main text). In later papers, Kohlrausch used the term “Wanderung” (Engl. migration) instead. Somewhat problematic for the reader of Kohlrausch's original works may be that he often changed terms during the four decades of his scientific activity. This is understandable, because, as we mentioned above, there was no standardized nomenclature. However, since this review is not intended to be a textbook of physical chemistry, we usually adopt the terms as Kohlrausch used it in the respective paper, unless they are completely misleading. In the cases where it could lead to confusion, we will use the modern terminology and symbols.

[52] It is hardly known that acids with 1, 2 and 3 $H^+$ ions and bases with corresponding $OH^-$ ions were called mono-, di- and triatomic until 1853, when Faustin-J. (also Faustino) Malaguti (1802 – 1878) proposed in his “*Leçons élémentaires de Chimie*” (ref. [129], p. 331) to call them mono-, di- and tribasic acids and mono-, di- and triacidic bases, respectively. It is still modern nomenclature.

experimental variables on the conductivity of electrolyte solutions till around 1910 (that is, please note, still in the *Long Nineteenth Century*). During this time period, he published almost 145 papers on this subject.

But first he continued work on his above-mentioned hypothesis for the next three years and published his results in 1879 on 120 pages of an ample paper that consisted of three parts.[130, 131] In theoretical Part III[130] he derived in detail the *law of independent ion migration*, which is also named 1st Kohlrausch law. In § 15 of this Part III he defined the quantity *m*, which he called the molecular content, as the number of electrochemical molecules per unit volume.[53] He defined the "moleculares Leitungsvermögen" (the molecular, later also molar conductivity), *k*/*m*, of the electrolyte in aqueous solution as conductivity, *k*, related to the molecular content, *m*. This quantity will be used by him in his future papers. Then, in § 18, he reported the remarkable finding of the similar difference in the molecular conductivities of two single-charged salts with a common ion. To give some examples: the difference for the pair *K* and *Li* is 274 for the chlorides, and 272 for the iodides; it is 160 for *K* and *Na* as chlorides, and 185 for their iodides; for the chlorides of *K* and $NH_4$ it is 21, and 14 for their iodides (all in the measure he used). These results encouraged him to formulate the final version of the *law of independent ion migration* in § 21, p. 168.[130] This derivation, expressed in modern notation, begins with the fact that the molar conductivity $\Lambda$ of an electrolyte solution is the sum of the molar ion conductivities, $\lambda_+$ and $\lambda_-$, of the two ions, i.e., $\Lambda=(\lambda_+ + \lambda_-)$.[54] To obtain the conductivity of the individual ions, Kohlrausch combined $\Lambda$, as indicated above, with the transference number, $\tau$, what led to the quested ion conductivity, e.g., for the anion as $\lambda_-=\tau_-\Lambda$, in which both, $\Lambda$ and $\tau_-$, are experimentally determinable measurands. Analogously, the cation conductivity is $\lambda_+=(1-\tau_-)$ or $\tau_+\Lambda$, because $(\tau_+ + \tau_-)=1$.

On p. 168, ref. [130] Kohlrausch formulated this *law of independent ion migration* (reproduced verbatim; note the almost identical wording of his 1876 hypothesis, that we quoted above, but which was, in contrast, formulated in subjunctive) as

> Hiernach muß also jedem elektrochemischen Elemente – z.B. dem H, K, Ag, …, Cl, J, $NO_3$,… – in verdünnter wäßriger Lösung ein ganz bestimmter Widerstand zukommen, gleichgültig aus welchem Elektrolyte der Bestandteil abgeschieden wird. Aus diesen Widerständen, welche für jedes Element ein für allemal bestimmbar sein müssen, wird sich das Leitungsvermögen jeder (verdünnten) Lösung berechnen lassen. (According to this, every electrochemical element – for example H, K, Ag, …,. Cl, J, $NO_3$,… – must feature a very definite resistance in dilute aqueous solution, regardless of which electrolyte the component is deposited from. From these resistances, which must be determinable for every element once and for all, the conductivity of each (dilute) solution will be calculable.)

He tested the validity of this theory by calculating the equivalent conductivity of the salts[55] by summarizing the tabulated conductivities of their ions (he completed his data with those from Robert von Lenz.)[126, 136],[56] Even after taking into account electrolytes with double-

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[53] We have already mentioned that, tedious for the current reader, Kohlrausch often changed the nomenclature and the phraseology during the long time of his researches. In this § 15 on p. 146 of ref. [130] he defined *m* as "*Die Anzahl der …. electrochemischen Molecüle, welche in der Volumeneinheit enthalten sind, werde ich kurz die Molecülzahl oder den Moleculargehalt der Lösung nennen und durch m bezeichnen.*" (*The number of …. electrochemical molecules contained in the unit volume, I will briefly call the molecule number or the molecular content of the solution and denote it by m*) It is a relative quantity, which is calculated "*Aus dem Procentgehalt und dem specifischen Gewicht bei 18° berechnet man die in 1 ccm Lösung enthaltene Milligrammzahl des Electrolytes und theilt letztere Zahl durch das electrochemische Moleculargewicht der Substanz.*" (*From the content in percent and the specific weight at 18°, one calculates the milligrams of the electrolyte contained in 1 ccm of solution and divides the latter number by the electrochemical molecular weight of the substance*). It clarifies the matter by Kohlrausch´s statement on pp. 172-173 in ref. [132] "*Die untersuchten Flüssigkeiten sind bezeichnet nach ihrem Gehalte an „electrochemischen Molecülen" (Aequivalenten) in der Volumeneinheit. Der „Moleculargehalt" m bedeutet …. die in 1 L der Lösung enthaltene Menge in Grammen, getheilt durch das Aequivalentgewicht A des Körpers. m = 1 bedeutet also die bei der Titriranalyse sogenannte „Normallösung.*" (*The liquids examined are designated according to their content of "electrochemical molecules" (equivalents) in the unit of volume. The "molecular content" m means … the quantity in grams contained in 1 L of the solution, divided by the equivalent weight A of the compound. m = 1 therefore means the "normal solution" as it is known in titration analysis.*) Later Kohlrausch called *m* the equivalent concentration (what Faraday named electrochemical equivalent concentration).

[54] We shall discuss in the following section that, taking into account the results of his research on the concentration dependence of conductivities, the modern notion of this equation reads $\Lambda^0=(\lambda_+^0+\lambda_-^0)$; superscript 0 indicates limiting conditions, that is, when the concentrations approach zero; see also, e.g., refs. [133][134][135]

[55] The concentrations of the salts were between around 5 weight % and their solubility limit, which reached for some salts about 80 weight %.

[56] The little-known Baltic-Russian physicist Robert von Lenz (1833, St. Petersburg -1903), son of the German-Baltic physicist Heinrich Friedrich Emil Lenz (1804, Dorpat, now Tartu, Estonia – 1865, Rome) known for Lenz's law in electrodynamics, was professor of physical geography at the University of St. Petersburg from 1865 to 1899. He published a paper in 1877, read in 1876, about conductivities of haloïd salts. Lenz´s conclusions there resembled Kohlrausch´s law of independent ion migration.[126][127] In 1879 he published conductivities of aqueous alkali salt solutions in the concentration ranges from about $10^{-1}$ to $10^{-3}$ equ.$L^{-1}$.[136] Notably, Lenz was the first who systematically determined transference numbers, conductivities and diffusion coefficients of ions in mixed aqueous-ethanolic solutions up to ethanol concentrations of about 94% (v/v). He confirmed the proportionality of conductivity and diffusion rate,[137] which was later expressed quantitatively (for limiting conditions) by the Nernst-Einstein equation.

charged ions, Kohlrausch found that the calculated values were in satisfactory agreement with the measured ones, considering the limited reliability of the transference numbers.[57] Eventually, Kohlrausch concluded

> In diesen Beispielen sehen wir unsere Vermuthung, dass die Beweglichkeit eines Jons in verschiedenen Verbindungen die gleiche ist, mit grosser Annäherung bestätigt. (In these examples we see our conjecture confirmed with great approximation that the mobility of an ion is the same in different compounds.)

Kohlrausch´s finding that ions migrate in the electric potential independent of the counterions was a milestone for the further development of the theories of ion migration.

### *The Concentration Dependence of the Conductivity, and the Conductivity at Limiting Conditions*

In the above chapter we have described Kohlrausch's first experiments in 1869 and 1870 on the conductivity of electrolyte solutions. This subject fascinated him so much that he introduced his next paper of July 1874 (the precursor of refs. [111, 112]) with the prophetic sentence: "*Diese in Gemeinschaft mit Hrn. Grotrian ausgeführte Arbeit soll den Anfang einer geordneten Experimental-Untersuchung über die Strom-Arbeit im Inneren der Elektrolyte bilden* " (*This work, carried out in collaboration with Mr. Grotrian, is to form the beginning of an orderly experimental investigation of the work of the current inside electrolytes*). This undertaking then actually extended over four decades. Following this stated intention, in 1875 and 1876 he investigated the resistance or conductivity of a large number of solutions of salts, bases, organic and inorganic acids and their dependence on the electrolyte content.[111-113, 144]

Their electrolyte concentrations ranged from full saturation down to a few percent by weight. Kohlrausch found a steady increase in conductivity with increasing concentration, with some electrolytes having a maximum at a particular concentration. For the discussion and comparison of the conductivities of the various electrolytes, he considered the indication of the concentration in percent by weight to be inappropriate. The conductivities of sulfuric acid and acetic acid, for example, could be determined at 100 %, while oxalic acid reached only 7 %, both (w/w). Note that also in 1876 he published the preliminary version of the law of independent ion migration (ref. [114], see previous section). These measurements were also carried out with solutions with electrolyte concentrations not lower than a few weight percent.[58]

### *The "Cubic-Root" Relation, the Precursor of the "Square-Root Law"*

In his paper from 1885 "*Ueber das Leitungsvermögen einiger Electrolyte in äusserst verdünnter wässeriger Lösung*" (*On the conductivity of some electrolytes in extremely dilute aqueous solution*)[132] Kohlrausch presented his measured conductivities in the low electrolyte concentration range between $10^{-5}$ and 1.0 mol.L$^{-1}$. He completed the actual data with those for molecular concentrations larger than 1 mol.L$^{-1}$ by his earlier ones and by those published by Long,[147] and obtained equivalent conductivities for concentrations up to nearly 10 mol.L$^{-1}$. Since it was not meaningful to plot the molar or equivalent concentration, $m$, in a linear scale over a range of about 6 orders of magnitude, he chose the cubic root of $m$ as the abscissa.[59] The resulting $k/m$ vs $m^{1/3}$ curves are shown in Figure 5.

Two shapes of these curves were clearly discriminable for Kohlrausch. He distinguished therefore two classes of electrolytes. Alkali salts of the type $A^+B^-$ were typical representatives of the 1st class. For these electrolytes, the $k/m$ values decreased only slightly by a few ten percent with increasing concentration in the low concentration range (Figure 5, upper scale). In contrast, 2nd class electrolytes like acetic acid and $NH_3$ exhibited a very low molar conductivity at high concentrations (pure acetic acid behaved as non-conductor). They remained at a low level when diluted over a wide concentration range, but rose steeply to values in the same range as those of the strong electrolytes when the solution became highly

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[57] Transference numbers with higher accuracy and with much less experimental effort than those by Hittorf´s method were later determined by the moving boundary method. This method will be discussed in a future paper together with electrophoretic separation methods in free solution. It was introduced in 1886 by Oliver Lodge,[138] and was further developed by W. C. D. Whetham,[139]. by O. Masson,[140] by A. Noyes,[141] by B. D. Steele and R. B. Denison,[142] and by others. It was theoretically clarified, in addition to other methods, in 1897 by Friedrich Kohlrausch with his "beharrliche Funktion" (the "persistent function", better known as "regulating function").[143] We will, however, not go into the details here.

[58] In 1868/69 also A. Paalzow measured the resistance of diluted salts and acids down to the low % range.[145][146] Rudolf Lenz reported conductivities of haloïd salts in 1877.[126][127] Later, experimental results and theoretical discussions about ion conductivities and their concentration dependence were published in 1880 by J. H. Long,[147] in 1884 by E. Bouty,[148][149][150] by Svante Arrhenius in his doctoral thesis,[151][152] which Kohlrausch provided with some pointed remarks, and by W. Ostwald.[153]

[59] Kohlrausch followed the suggestion of R. Lenz in 1878 to relate conductivity to the amount of electrolyte molecules in the solution.[136]

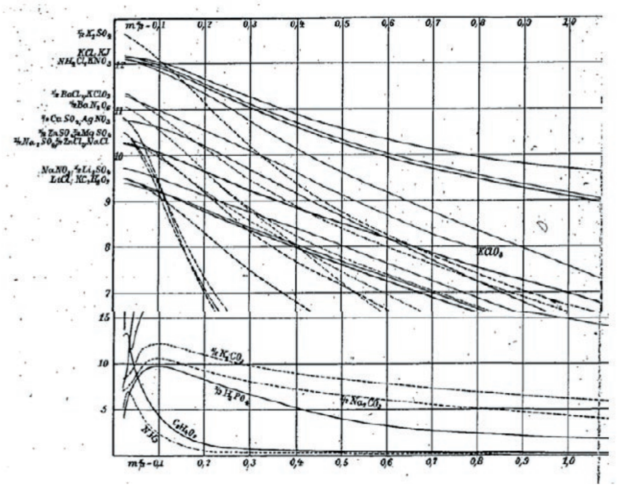

**Figure 5.** Equivalent conductivity ("specific molecular conductivity") as function of the cubic root, $m^{1/3}$ , of the equivalent concentration, $m$. The figure shows the left sectors of the total plot, that between zero and 1 equ.L$^{-1}$ concentrations. The curves were drawn exactly through the measured values. Upper scale, strong electrolytes, e.g. $KCl$, $KClO_3$, etc. Lower scale, concave two lowest curves: weak electrolytes acetic acid, $NH_3$. Modified; from ref. [132], Plate II, after p. 648.

diluted (see the two lowest and concave curves in the bottom scale of Figure 5.)

Kohlrausch recognized from the curves that the molar (or equivalent) conductivities of both classes of electrolytes nevertheless reached a certain limit at concentrations approaching zero.[132] He expressed $k/m$ as a function of $m$ for dilute solutions of strong electrolytes by the equation $k/m=A-Bm^{1/3}$. This relationship stated that the equivalent conductivity is proportional to the cubic root of the concentration, and under limiting conditions it is equal to constant value $A$. For salts from single-charged ions, if only for these, the curves were approximately linear up to the concentration range of 1 mol.L$^{-1}$ (see, for example, that for $KClO_3$ in the figure). Kohlrausch interpreted this dependence by the assumption that $m^{1/3}$ corresponds to the reciprocal mean distance between the electrolyte molecules. For the 2nd class electrolytes he had no coherent explanation. This cubic root equation, which applied to a relatively large range of concentration, preceded Kohlrausch´s "square-root" equation for extremely dilute solutions which will be discussed in the following.

After the investigations in 1885 Kohlrausch was aware of the insufficient accuracy of the data measured so far, as he assessed their quality as too low for the formulation of a sound and general theory, especially with regard of the values at very low concentrations. He therefore tried to identify and reduce the possible sources of errors. This was the goal of his comprehensive and elaborate studies over the next years.

**Figure 6.** Photograph of Friedrich Kohlrausch´s research group at the Physical Institute of the University in Würzburg in winter semester 1886/87, taken in February 1887. Standing from left, Adolf Heydweiller, Ewald Rasch, Svante Arrhenius (research visit in Würzburg in 1886/1887), Walther Nernst. Sitting from left, Wilhelm Kohlrausch, Friedrich Kohlrausch, Samuel Sheldon (postgraduate; 1887-1888). Source of photograph: Ernst H. Riesenfeld. Svante Arrhenius. Akademische Verlagsgesellschaft, Leipzig, 1931. Public domain.[154]

In Figure 6 a photograph of Friedrich Kohlrausch´s group at the University in Würzburg in 1887 is shown. It was taken when Kohlrausch was visited by Svante Arrhenius, who published in this year his seminal dissociation theory *"Ueber die Dissociation der in Wasser gelösten Stoffe"* (*On the dissociation of substances dissolved in water*).[155],60 Although Arrhenius' theory provided the explanation for the deviating dependence of the 2nd class electrolytes such as acetic acid, Kohlrausch was skeptical of it. He continued to focus on strong electrolytes at limiting conditions, preferably on those with single-charged ions.

In strict chronological order we had now to proceed with Arrhenius' dissociation theory from 1884.[151, 152]. However, we prefer to continue systematically with Kohlrausch's electrochemical work after 1887,[61] and will

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[60] Arrhenius completed his doctoral thesis in 1884. It was published in two parts of "*Recherches sur la conductibilité galvanique des électrolytes*."[151][152] In 1887, his dissociation theory was published in the first volume of *Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre*,[155] founded by Wilhelm Ostwald and Jacobus Henricus van `t Hoff. In 1928 its title was changed to *Zeitschrift für physikalische Chemie*. Arrhenius' theory fundamentally changed the previous conception of the behavior of electrolytes in solutions, and was a decisive step in the development of modern physical chemistry. In 1903 he became the first Swedish Nobel laureate.

[61] It should be noted that in 1889 and 1890, due to adverse circumstances, Kohlrausch did not publish a single paper.

return to Arrhenius' theory and its pioneering consequences in the following, separate Part 4 of our series.

### *The "Square-Root" Law: 2nd Kohlrausch Law*

In order to achieve the proverbial high accuracy of his experimental results, for which Kohlrausch was famous, he examined step by step the effects of possible causes of errors. He tried to reduce the total systematic error at conductivity of solution with molecular concentration of 0.0001 which required errors in conductivity one magnitude lower in each individual step at molecular concentrations of 0.00001. We list a part of the subjects of these studies in condensed form in footnote [62], along with the articles in which they were published. It turned out that two sources of errors were most problematic. One was the well-known polarization of the electrodes, a problem Kohlrausch solved, as he had done earlier, by using alternating rather than direct current. He used, in addition, an improved apparatus, the Wheatstone bridge, for the measurement of the resistance.[63]

The second problem was that the water used as a solvent had to be of very high purity. Kohlrausch's coworker Adolf Heydweiller countered this problem in 1894 with cumbersome and time-consuming purification processes.[158, 172]

In their paper from 1900, Kohlrausch and his coworker E. M Maltby published very accurate conductivities of alkali halides and nitrates in highly dilute solutions in a comprehensive report which covered eighty printed pages and summarized the results of their elaborate investigations.[133] Taking the data at lowest $m$ between $1.10^{-5}$ and $4.10^{-5}$ equ.$L^{-1}$ (out of a set over a range of up to 1 equ.$L^{-1}$) Kohlrausch expressed the dependence of the equivalent conductivity, here symbolized by $\Lambda$, on $m$ by the equation $\Lambda_0$-$\Lambda$=$Pm^{1/2}$; $\Lambda_0$ and $P$ are electrolyte-specific constants.[133],[64]. He called this equation "Quadratwurzel Gesetz" (literally "square root law", better known in English literature as 2nd Kohlrausch law).[65] The equation signifies the linear dependence of the equivalent conductivity of the electrolyte on the square root of its equivalent concentration, and again applied especially for strong electrolytes with single-charged ions. The intercept $\Lambda_0$ represents the limiting equivalent conductivity of the electrolyte at concentrations $m \rightarrow 0$. Constant $P$, the slope of the line, depends mainly on the stoichiometry of the respective electrolyte. Note that the concentration to the power of ⅓ in the equation in his paper from 1885[132] is substituted here by the power of ½, because the former applied for a much larger concentration range. The decisive factor for the better agreement of the $m^{1/2}$ – relationship was not the lower measurable concentration of the electrolytes, it was the higher accuracy of the conductivity data at these extremely low concentrations. We illustrate this excellent relationship in Figure 7,[135] when Kohlrausch had available a larger number of more accurate data.[66]

The following paper of 1907 is a kind of résumé of Kohlrausch´s electrochemical contributions; in it he reconfirmed his earlier works. He subjected his theories of independent ion migration and those of conductance and mobility at limiting conditions to his own criticism. Moreover, he reaffirmed the validity of his square root law from 1900[133] not without emphasizing that this law applies only to salts of single-charged ions, and to concentrations not higher than a few $10^{-5}$ mol.$L^{-1}$. For higher concentrations this dependence is represented – as described in the above chapter – by the cubic root equation.[133] Kohlrausch also mentioned the alternative equations by Max Rudolphi[173] and J. H. van ´t Hoff,[174] which read in his version $(\Lambda_0\text{-}\Lambda)/\Lambda^p = C\eta^{1/2}$. Exponent $p$ was taken as 2 by the former, and 3/2 by the latter author; $\eta$ is here the equivalent concentration. Kohlrausch pointed out that these equations, however, apply only to individual cases. In 1908 he published three

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[62] (▪) Influence of solubility of glass ware in contact with the solutions on the conductivity; ascertaining threshold level of conductivity of pure water used as solvent.[156][157][158] (▪) Corrections taking into account temperature coefficients of water and of solutions, comparison with previous measurements.[132][159] (▪) Estimation of deviations of electrolyte concentrations upon contraction by mixing of solutions and by evaporation of solvent.[160] (▪) Measurement of resistance of electrolyte solutions with direct and alternating current.[161][162][163][164] (▪) Density measurements of dilute electrolyte solutions.[160][165] (▪) Determining and improving the properties of rheostat, capacitor and Wheatstone bridge.[166]. (▪) Specification and improvement of quality of resistor cells and electric wiring.[167] (▪) Investing effect of polarization of platinized electrodes in measuring cell.[168][169] (▪) Calibration of thermometer to 0.01° instead of common 0.1° (§ 15) and of the volumina of graduated measuring glassware (§ 16, volumetric flasks; § 18, pipets) in ref. [133]

[63] The principle of the device called Wheatstone bridge was initially described by the British mathematician and physicist Samuel Hunter Christie (1784, London – 1865, Twickenham, London) and reported in 1833 in his Bakerian Lecture "*Experimental Determination of the Laws of Magneto-electric Induction in different masses of the same Metal, and of its Intensity in different Metals*."[170] It was not noted until Charles Wheatstone presented it ten years later, mind you, as Christie's invention, in his Bakerian lecture "*An Account of Several New Instruments and Processes for Determining the Constants of a Voltaic Circuit.*"[171]

[64] In this concentration range the conductivity of water (purified by up to 40 to 50 distillations under vacuum from a quartz apparatus)[158] was about one order of magnitude lower than those of the highest diluted electrolyte solutions.

[65] Remember that the 1st Kohlrausch law is the law of independent ion migration.

[66] The data were taken from sources Kohlrausch cited in footnote 3, p. 336, ref. [135]

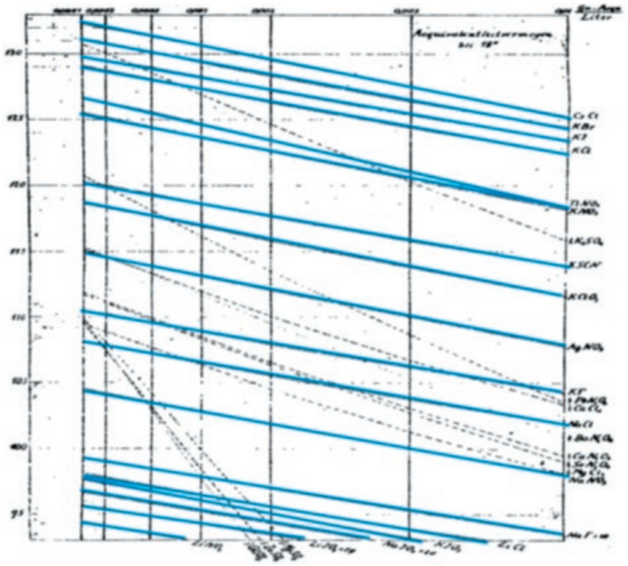

**Figure 7.** Dependence of the equivalent conductivity on the square root of the equivalent concentration according to the 2nd Kohlrausch law, the square-root law (termed "Quadratwurzel Gesetz" by Kohlrausch) for 1st class electrolytes. The straight lines of electrolytes with the same stoichiometry run parallel, most pronouncedly for salts with 1:1 single-charged ions. They are highlighted in blue. Since the letters in the illustrations of that time were mostly very small and hardly legible, we give the formulas of these salts in the order from top to bottom as follows: *CsCl*; *KBr*; *KCl*; $KNO_3$; *KSCN*; $KClO_3$; $AgNO_3$; *NaCl*; *NaF*; *LiCl*; $KJO_3$; $NaJO_3$; $LiJO_3$; $LiNO_3$. Ordinate, equ. conc.; abscissa, equ. conductivity. Modified, from [135].

more papers on electrochemistry, mainly on temperature effects of electrolyte solutions, and on January 4, 1910 he submitted a paper on "*Practical Rules for Number Corrections, Namely for the Transition to Other Atomic Weights*".[175] He died on January 17, 1910.

### *Migration Velocity and Mobility of ions*

The question about the absolute migration velocities of the ions, not only about their relative values, has been systematically treated by Kohlrausch in several papers. [114, 130, 159, 176] In 1893 he had available improved values of the conductivity in dilute solutions, a valuable addition of Hittorf´s transference numbers, more reliable values for the electrochemical equivalents and the absolute resistance of mercury. Therefore, he was able to calculate more accurate data "*Ueber die Geschwindigkeit elektrolytischer Ionen*" (*On the velocity of electrolytic ions*).[159] He limited the following calculation to strong electrolytes, from which he could be convinced that the molecules completely decompose to ions (we recall that Arrhenius dissociation theory was published as journal article in 1887). We place his derivation into footnote [67] and add only the result after transformation into modern system of units and terminology.

Kohlrausch derived an equation for the migration velocities at unit field strength, that is to say, at 1 V.cm$^{-1}$, which he called "Beweglichkeiten" (mobilities), and which are, after multiplied by the according factor, the migration velocities in cm.s$^{-1}$. By transformation this mobility reads $\mu_i=\lambda_i/F$, at limiting conditions $\mu_i^0=\lambda_i^0/F$, and is today also called mobility of ion, *i*. Here $\lambda_i$ is the molar ion conductivity, and $F$ the Faraday constant. The velocity $v$ in $cm.s^{-1}$ at field strength $E$ is accordingly $v_i= \mu_i.E$.[68]

Ion mobilities $\mu_i$ are of decisive importance in all variants of capillary electrophoresis in free solution. They are ion specific parameters that are independent of the potential. They depend on temperature, on electrolyte concentration (more precisely, on ion strength, what was unknown at that time) and on the solvent.[69]

Since the migration velocity can be derived from the known ion conductivity and the chosen field strength, the question posed in this Part 3 about its magnitude can be regarded as answered.

However, the reason for its dependence on experimental variables, especially on their concentration, was still unknown at that time.

The reader will probably note that we have not yet addressed the main question of whether or not electrophoresis experiments in free solution were performed in devices of capillary format in the years under consideration. For this reason, we conclude the present essay by describing the first use of capillaries in electrophoresis and additionally mention that all experiments cited below were performed with direct current.

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[67] Kohlrausch derived the velocities for single-charged 1:1 electrolytes, that is, the molar and equivalent concentrations are the same. He considered a solution with molar concentration *m* of the electrolyte, which has the conductivity, *k*, and the "molecular conductivity" *k*/*m*, which is the sum of the molar conductivities of anions and cations. He derived the migration velocities of the ions at a potential difference of 1 V.cm$^{-1}$. He first changed conductivity *k* from its relationship to mercury to Ohm. He calculated the current in Amp. at 1 V.cm$^{-1}$ in 1 cm$^3$ of electrolyte solution with *m* mol.L$^{-1}$ concentration, and derived the number of moles electrolyzed by this current. This quantity is released at the electrodes at a distance of 1 cm. From this he derived the sum of the mean velocities of cations and anions and obtained those of the two ion species using Hittorf´s transference numbers. The resulting equation expressed the ion migration velocity in cm.s$^{-1}$, mind you, at a potential difference of 1 V.cm$^{-1}$, as a function of the molar ion conductivity. Readers who are interested in the specific numerical data in this derivation are referred to pp. 402-403 in ref. [159]

[68] In modern notation the migration velocity $v$ is in $cm.s^{-1}$, the mobility $\mu$ in $cm^2.V^{-1}.s^{-1}$ or $S.cm^2.A^{-1}.s^{-1}$, and the molar ion conductivity in $S.cm^2.mol^{-1}$.

[69] Other researchers determined migration velocities of ions in the time period under consideration as well by the moving boundary method. We mentioned them in footnote[57].

## THE FIRST CAPILLARY ELECTROPHORESES OF IONS

At the outset of this particular chapter in the history of electrophoresis, it should be made clear again that electrophoresis is not limited to the separation process as which it is generally regarded today, as already stated in footnote [1] in the introduction to this article. The history of capillary electrophoresis must therefore be considered from this point of view. To maintain continuity with the preceding narrative, we follow up the previous section with Kohlrausch's research around 1900 and address the topic in reverse chronological order.

### *1895. F. Kohlrausch and A. Heydweiller*

In the course of their investigations on pure water in 1894[158] Kohlrausch and his coworker Adolf Heydweiller observed that after applying direct current the electrical resistance of water decreased rapidly. Changes in resistance were also observed in normally distilled and in highly distilled water and in some dilute aqueous salt solutions. Switching the current off and on resulted in some cases first in a decrease, after some time in an increase of the conductivity; in other cases, the reverse sequence was observed. One can follow their explanations of the reasons for these effects[70] in their paper "*Ueber Widerstandsänderung von Lösungen durch constante electrische Ströme*" (*On the change of resistance of solutions at constant electric currents*)[163] published in 1895. But this is of minor interest here.

Much more relevant to the issue at hand, they conducted their experiments in narrow open tubes of capillary dimensions because the zone boundaries described in footnote [70] were much sharper there than in tubes of larger diameters. They therefore used U-shaped capillaries with lengths of a few cm and inner cross-sectional areas of 1 mm$^2$ and 0.6 mm$^2$, that is, with radii of 560 and 440 µm. Kohlrausch and Heydweiller thus performed capillary electrophoresis – mind you – of ions. But they were far from being the first to introduce this method.

### *1889. W. Ostwald and W. Nernst*

We recall that Clausius' theory of free ions from 1858 was proved by Kohlrausch's 1869 experiment using thermoelectricity[107] as described in the chapter above. In 1888, Wilhelm Ostwald had theorized that free ions must be present in an electrolyte solution, otherwise the principles of electricity would be violated.[178] In 1889, together with Walter Nernst, he caught up with the experimental confirmation of his theoretical paper and described it in "*Ueber freie Ionen*" (*On Free Ions*).[179]

Ostwald and Nernst used an apparatus similar to Lippmann's capillary electrometer.[71] They modified the simplest version of this instrument, which is depicted in Fig. 3 on p. 503 of ref. [180]. In short, they took a tube of several tens of centimeters in length and reduced its lumen at one end to a capillary of 3,7.10$^{-3}$ cm inner radius. They fixed the tube vertically, poured mercury into it, and immersed the tip of the capillary in dilute sulfuric acid. Then they sucked the mercury together with the acid into the middle of the capillary length. A platinum wire served for connection with the mercury. Next, they took a glass flask, covered with tin foil and filled with dilute sulfuric acid. This solution was connected to the acidic solution in the capillary via a wet thread. The mercury was grounded, and the positive pole of a small electrifying machine was connected to the outer tin foil of the flask. As soon as the machine was set in motion, the mercury meniscus promptly raised, indicating a potential difference between the two electrodes.

Remarkably, gas bubbles were formed, dividing the mercury in the capillary at several points. The authors explained this effect as follows. When the tin foil of the flask becomes positively charged, the negative sulfate ions are attracted, while the positive hydrogen ions are repelled. The latter travel through the wetted threat to the solution in the capillary and then through the platinum wire from the mercury to ground. The hydrogen transfers its electricity to the mercury in the capillary and appears as hydrogen gas.

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[70] They related it, for example, to the reaction of the solutions at the electrodes and the migration of boundaries of $H^+$ or $OH^-$ formed by electrolysis from the one to the other electrode. Such effects were called by G. Wiedemann "*Ausbreitung der freien Säure vom positiven Pol aus*" (*Propagation of the free acid from the positive pole*), ref. [39], p. 167, and by H. Buff "*Ausbreitung der Säure gegen den negative Pol* " (*Propagation of the acid towards the negative pole*), ref. [177], p. 171. When both boundaries meet one another, neutralization takes place, water is formed, and the conductivity of the solution decreases. Kohlrausch and Heydweiller could visualize the motion of the boundaries by adding acid/base indicators.

[71] Lippmann's capillary electrometer enabled the measurement of very small numbers of electrical charges, and of potential differences down to a few tens of µV. Its main part consisted of a capillary half filled with liquid mercury in direct contact with a dilute solution of sulfuric acid. Both are connected with wires that serve as electrodes. Its principle is based on the relationship between the surface tension, the surface charge density of the mercury and the potential difference of the electrode points. Expressed by the Lippmann-Helmholtz equation, the surface tension of mercury is directly related to its surface charge density. A change in the potential difference leads to a change in the surface charge density, which in turn changes the surface tension. This causes the mercury meniscus in the capillary to rise or fall, which can be accurately measured using a microscope and, after calibration, gives the potential difference between the two electrode points.

Ostwald and Nernst argued that the motion is caused by influence, also known as electrostatic induction, and the formation of hydrogen on the mercury is clear evidence that decomposition has occurred. Since electrolysis does not occur without electrophoretic ion migration, the authors claimed that it was free ions that were moving. They also argued that only their explanation was consistent with the laws of thermodynamics (p.125 ff.). Taking this explanation as fact, Ostwald and Nernst performed capillary electrophoresis – again, mind you – of ions, six years before Kohlrausch and Heydweiller.

### *1865. W. Beetz*

The German physicist Wilhelm Beetz[72] had already done research in this field in 1862, albeit with wider tubes, namely one with 13.4 mm i.d. and 297 mm length, the other with 6.2 mm i.d. and 207 mm length;[116] numbers rounded by us. His attention was drawn to the 1861 work of Edmond Becquerel on the conductivity of electrolyte solutions in capillaries,[181] which we will discuss in the next section. Beetz recognized that the conclusions in his work differed in part from Becquerel's. Doubting Becquerel's results, he decided to extend his measurements in 1865 from wide tubes to capillaries.[182] Thus, for comparison, he measured the resistances and calculated their reciprocal, the "Leitungsfähigkeiten" of electrolyte solutions in these capillaries.

For this purpose, Beetz constructed a device equipped with two Grove elements and determined the conductivities of zinc sulfate solutions with non-polarizing amalgamated zinc electrodes, and in six capillaries. The capillaries were between 77.7 and 161.2 mm long and had cross-sectional areas between $28.10^{-3}$ and $89.10^{-2}$ $mm^2$ (derived from the weights of the mercury-filled tubes), corresponding to inner diameters between 190 and 690 µ*m*; all numbers rounded by us. Beetz found that the resistances are directly proportional to the lengths of the capillaries, and are inversely proportional to the cross-sectional area of the capillaries.

### *1861. The Priority: Edmond Becquerel*

In 1846 and 1847, the French physicist Edmond Becquerel[73] published the result of his investigations of the conductivity of electrolyte solutions that were filled in tubes with centimeter dimensions of inner diameter and length. In these works[184-186] he tested whether the relations of lengths and cross sections, as he had found in metal wires, also applies in electrolyte solutions.[74]

In the April 1861 issue of *Annales du conservatoire des arts et des métiers*, he published an essay with the designative title "*Études sur la conductibilité des liquides dans les tubes capillaires rhéostat destiné à la comparaison des grandes résistances*" (*Studies on the conductivity of liquids in capillary tubes; rheostat for the comparison of large resistances*".[181] In this paper he reported conductivities of liquids, but measured in capillaries of different inner diameters for comparison with resistances of metallic wires.

The device Edmond Becquerel constructed and used for his measurements in capillaries is presented in Figure 8. We describe in the following only the right one of the two glass tubes shown, because the other, similar measuring system had the same characteristics and was installed only for control and comparison. And it is described in more detail because – to the best of the author's knowledge – it was the first instrument ever used to perform capillary electrophoresis of ions in free solution.

The device consisted of a glass tube (*AB*) closed at the bottom and open at the top, with a diameter of 2 to 3 cm and a height of 50 to 60 cm. It was placed vertically in a larger glass vessel (*MN*) with 20 cm diameter and a height approximately equal to that of the tube. Water was filled into the large vessel to maintain the test solution, an aqueous solution of an electrolyte, at constant temperature. The tube was filled with the solution whose conductivity was to be determined. A capillary (*GH*) with a constant inner diameter and open on both ends, scaled in half-mm increments, was inserted in the axis of the tube and fixed there. The test liquid was filled into the tube and penetrated into the capillary, forming a narrow column of the electrolyte solution inside. Then a metal wire, (*cd*), made from copper, zinc, silver, or platinum, the type of which depended on the test solution,

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[72] Wilhelm von Beetz (1822, Berlin – 1886, Munich) studied physics and chemistry in Berlin from 1840. From 1850 he was professor of physics at the Cadet Corps and at the Artillery and Engineering School in Berlin, from 1855 professor in Bern, from 1858 in Erlangen and from 1868 professor at the Technical University in Munich. His main field of research was electricity, especially topics of electrical conductivity of liquids.

[73] Edmond Becquerel, together with his father Antoine-César Becquerel, discovered in 1839 a variant of the photoelectric effect, later called the Becquerel effect. His main areas of research were phosphorescence of light and its chemical effects. He also investigated topics in optics and electricity. He is the father of Nobel Laureate (Antoine) Henri Becquerel. For a detailed biography of Alexandre-Edmond Becquerel (1820, Paris – 1891) see C. Blondel, ref. [183].

[74] It is remarkable that all authors discussed so far completely ignored Gustav Theodor Fechner´s comprehensive contribution about the validity of Ohm´s law for electrolyte solution, which he reported in his book "*Massbestimmungen über die galvanische Kette*".[69] He published the same findings already in 1831, see his conclusions formulated in points (i) and (ii) in Chapter "Leap in Time" above. Fechner, however, did not carry out his measurements in capillaries.

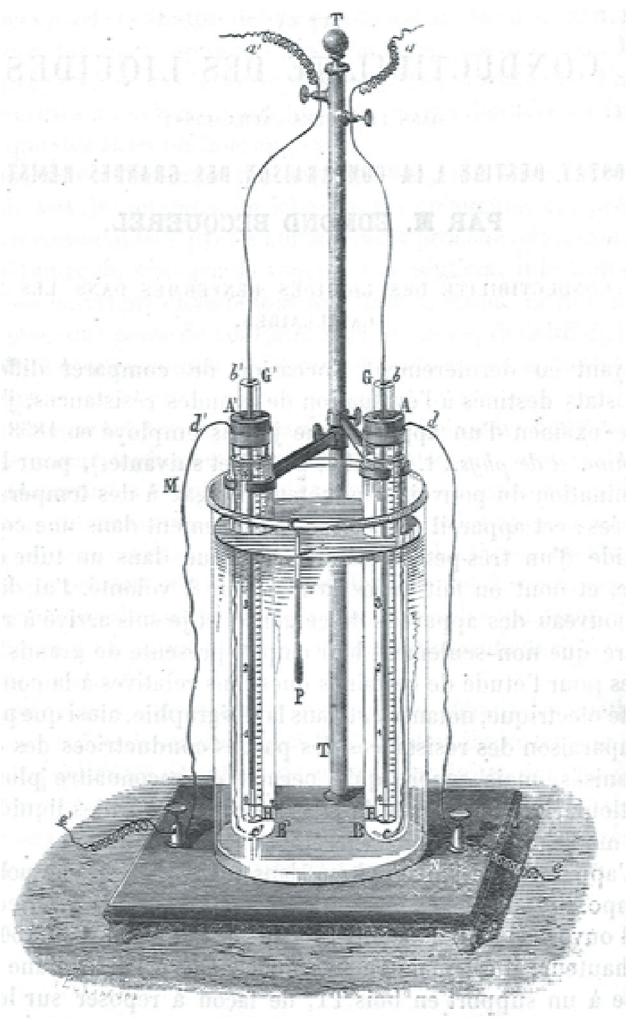

**Figure 8.** The rheostat constructed by Edmond Becquerel in 1861 for the first capillary electrophoresis of ions.[187] Explanations are included in the main text. Reproduced from Cnum – Conservatoire numérique des Arts et Métiers – http://cnum.cnam.fr with permission.

were inserted into the tube (*AB*). The end of the wire in the tube was placed near the bottom of the capillary (*GH*). The diameter of the other wire, (*ab*), which was inserted into the capillary from its upper opening, was very close to the inner diameter of the capillary, and acted like a piston. By pressing this wire, the length of the liquid column of the test solution in the capillary could be varied and its position could be measured on the calibrated scale with a magnifying glass.

The metal wires, (*cde*) and (*ab*), were connected to a Bunsen battery consisting of one to ten elements.[75] With this arrangement, the current was forced to flow through the test solution inside the capillary, the length of which could be varied by hand by the wire. The current was measured with an astatic galvanometer. By using capillaries with different cross sections the resistance and the conductivity of the electrolyte solution in dependence on the liquid length and its diameter could be determined. Five different capillaries were used with lumen radii of 929, 478, 238, 229 and 183 $\mu m$. Polarization was minimized by using wires of the same metal as the cations of the test solutions.

Becquerel found that the resistance of such a liquid thread in a capillary is in direct proportion to its length, which is consistent with theory. However, he found that the product of resistance and the square of the inner diameter varied with decreasing diameter (of capillaries with the same length), and differed from that calculated for the given diameter (see Plate on p. 741).

On the one hand, Beetz agreed with Becquerel´s first conclusion. In contrast to Becquerel, however, Beetz found the resistances to be inversely proportional to the cross-sectional area of the capillaries, that is, the product of resistance and cross-sectional area is constant for capillaries of a given length. Beetz´s results were in agreement with the present theory, and also with Fechner´s early findings (see Chapter "Leap in Time"). Beetz's conclusions were plausible, and he had good reasons to explain the deviations from Becquerel's results, which he attributed to improper experimental conditions.

We note that Edmond Becquerel measured the conductivities, no matter whether right or not, and thus the migration properties of dissolved ions in an electric field, i.e., he actually performed electrophoresis. Even more, he was (as far as we know) the first to apply electrophoresis in capillaries – again, mind you – of ions.

It is noteworthy that the first capillary electrophoresis of colloidal or coarse-grained particles was performed around the same years, 1860 and then 1861, a fact we highlighted in the introduction to Part 1 of our series.[1] We will report in detail on this first capillary electrophoresis of colloidal particles in a later article. However, perhaps surprisingly, this will not be the work of either Nicolas Gautherot or Ferdinand Friedrich von Reuß, as they did not use capillaries in their discoveries.

## SUMMARY

Around 1840, it was generally believed that the ions of strong electrolytes, like those of salts, migrate in solu-

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[75] A Bunsen element was invented by Robert Bunsen in 1841.[188][189] It is an electrochemical zinc-carbon cell with zinc as anode in dilute sulfuric acid, which is separated from a carbon cathode in nitric or chromic acid by a porous pot. A single element delivers an electric potential of about 1.9 V.

tions at the same electrophoretic velocity toward their respective electrodes, a view shaped by the theories of Th. von Grotthuß, H. Davy, and M. Faraday. However, this view was challenged by the results of recent experiments, which had shown that the solutions of some strong electrolytes after electrolysis had different concentrations near the two electrodes, in the so-called electrode compartments. These findings were incompatible with the established theory. Wilhelm Hittorf drew his conclusions from these observations and argued that the earlier view was based on a fallacy. Instead, he derived a hypothesis according to which anions and cations actually move electrophoretically at different speeds. In his opinion, concentrations can only differ if one type of ion migrates faster than the other. He related the change in concentration in the electrode compartments to the current that an ion type transports relative to the total current which flows during electrolysis. He termed this fraction of the current, which is equal to the ratio of the velocity of a particular ion to the sum of the velocities of both ion species ”Überführungszahl", i.e., transference or transport number of an ion in a given electrolyte. Regrettably, the transference number expressed only the velocity of an ion relative to its counterion, but did not give the magnitude of the absolute velocity.

At the end of the 1860s, Friedrich Kohlrausch began researching the conductivity of electrolytes, a topic that would subsequently occupy him throughout his life. He found that conductivity decreased with decreasing concentration of the electrolyte, but more relevant to him were the conductivities normalized to their concentrations. He observed that the ratio $k/m$ of conductivity, $k$, and the equivalent or molar concentration, $m$, of the electrolyte increased with increasing dilution. He quoted $k/m$ as the equivalent and molar conductivity, in modern notation, $\Lambda$,[76] the quantity which turned out to be central for his further research.

Kohlrausch found that two types of electrolytes can be distinguished. With strong electrolytes, such as neutral salts, the value k/m decreased only slightly with increasing concentration. With weak electrolytes such as acetic acid and ammonia, on the other hand, there was no such dependence, since k/m remained at low values at low dilutions but rose steeply within a certain narrow range of decreasing concentration.

He subsequently focused his research on strong electrolytes in very dilute solutions, preferably but not exclusively on those consisting of single-charged ions. He was able to show that ion and counterion of an electrolyte migrate independently of each other and that an ion, regardless of which electrolyte it comes from, always has the same "molecular" – now molar – ion conductivity. This was the law of independent ion migration, also quoted as the 1st Kohlrausch law, which he derived in 1879. In determining $\Lambda$ at different concentrations, Kohlrausch formulated an empirical law which stated that $\Lambda$ decreases linearly with $m^{1/2}$ for very dilute solutions. It is known as the 2nd Kohlrausch law and was called by him the "Quadratwurzel Gesetz (square root law). The extrapolation of the ion concentration to limiting conditions, i.e., to concentrations approaching zero, led to an ion-specific and concentration-independent variable, the limiting ion conductivity. It is little known that the 2nd Kohlrausch law was preceded by the relationship between $\Lambda$ and the cubic root, $m^{1/3}$, which applied to a larger concentration range.

The ion velocities and their mobilities, that is, their drift speed at a unit field strength, could be calculated by Kohlrausch by combining Hittorf´s transfer numbers with conductivity data and the law of independent ion migration. However, their knowledge did not contribute to a deeper understanding of the form in which ions exist in solutions.

It also did not indicate how they drift in the electric field trough the solution, although a connection with the viscosity of the solution and with the frictional resistance has already been assumed. It must be remembered that the generally accepted concept before the late 1880s was not very different from the one introduced by von Grotthuß about eight decades ago. It was still based on the conjecture that an ion only exists in solution in an electrically neutral assembly with a counterion, which needs an electric field to divide. Rudolf Clausius, on the other hand, argued in 1857 that ions in solutions exist in free form as a result of their thermal energy even in the absence of an external electric force, although, as he assumed, only to a small extent.[77]

We do not wish to diminish the significant contributions of many other scientists to ion migration, but it would not be appropriate to quote names selectively. Certainly we must cite the early contributions of G. Fechner, but also refer to the later measurements of ion migration velocities by those mentioned in footnote [57] who mainly used the moving boundary method for their determinations.

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[76] For the sake of better readability, we replace the written terms by symbols and restrict ourselves to strong 1:1 electrolytes with single-charged ions. The molar conductivity of the electrolyte solution is $\Lambda$, that of the ion species $\lambda$. The molar concentration is symbolized by $m$.

[77] This latter aspect of Clausius´ theory, the low fraction of free ions, was retrospectively disproved in 1889 by Wilhelm Ostwald and Walter Nernst in their paper entitled "*Über freie Ionen*" (*On free ions*) by the conflictive consequences to the law of thermodynamics and by subtle experiments.[179]

However, we consider Kohlrausch a key figure in the field, having done pioneering work for more than four decades, longer than others, although his greatest achievements in the field of electrophoretic properties were ultimately in the area of strong electrolytes. At the end of Kohlrausch's research, which lasted until about 1910, two questions remained unanswered for him. The first question was why the values of strong electrolytes increase with increasing dilution to a limit at concentrations close to zero. Kohlrausch hypothesized that under the limiting, but only under these conditions, possible ion-counterion interactions tend to cease completely. But the second open question, namely why compounds of the 2nd class, weak electrolytes like acetic acid, deviate so much from the usual behavior of the strong electrolytes, could by no means be answered conclusively with this assumption.

The answer to the first question was given at the begin of the *Short 20th Century*[78] by Lars Onsager,[190, 191] based on the theories of Peter Debye and Erich Hückel.[192, 193] But Kohlrausch could have seen the solution to the second problem as early as the 1890s, if he had not been so skeptical of the theory of electrolyte dissociation Svante Arrhenius published in 1887. In fact, this dissociation theory not only provided the plausible answer to this second question but moreover, represented the next, major step toward the modern physical chemistry of electrolyte solutions. This pioneering theory and its consequences in the last decades of the *Long Nineteenth Century*, or, as we term it, the "*1st period of electrophoresis*," which ended in 1914 with the first utilization of electrophoresis as a method for separating compounds in mixtures will be the subject of the following Part 4.

We attach great importance to close this chapter of scientific research not without pointing out that electrophoresis of ions in free solutions in capillaries was performed for the first time in its history in the second half of the *Long Nineteenth Century*, in four times between 1861 and 1895. The last time this happened was in 1895, when F. Kohlrausch and A. Heydweiller applied direct current instead of alternating current to liquids filled in glass capillaries and observed the movement of the boundaries of ion zones caused by unexpected resistance changes. One could speculate whether this phenomenon led him to derive his important "beharrliche Funktion" in 1897, the "regulating function". In 1889, W. Ostwald and W. Nernst investigated whether free ions are present in solutions according to Clausius' theory. They used the capillary of a Lippmann electrometer for their experiments. In 1865, W. Beetz investigated ion migration in capillaries because he doubted the results of Edmond Becquerel, who wanted to compare the conductivities of liquids in capillaries with those of metal wires. In any case, it is recognized that the priority is owned by Edmond Becquerel, since he first performed capillary electrophoresis of ions as early as 1861.

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[78] The "*Short Twenties Century*," popularized by the noted British historian Eric Hobsbawm (1917 – 2012) in his book *The Age of Extremes*, covers the period between the beginning of World War I in 1914, i.e., at the end of the *Long Nineteenth Century*, until the beginning of the collapse of the USSR in 1989. For details, see Part 1 of our review series.

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