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## Capillary Electrophoresis and its Basic Principles in Historical Retrospect. Part 4. Svante Arrhenius' Electrolyte Dissociation. From 56 Theses (1884) to Theory (1887)

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**Abstract.** Since the main interest of Svante Arrhenius, a student at Uppsala University, was the electrical conductivity of highly dilute electrolyte solutions, which had not yet been determined at the beginning of the 1880s, he decided to determine experimentally the molecular conductivities of aqueous solutions of about fifty electrolytes and their dependence on the dilution. In his dissertation, which he began in the winter of 1882/1883, he summarized his results and considerations in 56 “theses”. He observed that strong acids had a high molecular conductivity, which increased only slightly with increasing dilution. Weak acids, in contrast, had low molecular conductivities, but these increased abruptly above a certain dilution. Arrhenius' innovative hypothesis was that electrolyte molecules are composed from two parts, “an active (electrolytic) and an inactive (non-electrolytic) part,” with the proportion of the active part increasing with increasing dilution at the expense of the inactive part. Moreover, the electrically active part, which conducts electricity, was also the chemically active part. Arrhenius introduced the activity coefficient, later quoted as the degree of dissociation, which indicated the proportion of active molecules to the sum of active and inactive molecules. He tentatively related activity coefficient to molecular conductivity. He assumed that the higher the activity coefficients of different acids at the same equivalent concentrations, the stronger they are. Arrhenius tested his hypothesis taking the heat of neutralization of acids with a strong base measured by Thomsen and Berthelot. Strong acids developed the highest neutralization heats, i.e., the activation heat of water, since they consisted entirely of active  $H^+$  and  $OH^-$  ions, which combined to inactive  $H_2O$ . Weak acids developed correspondingly less. The established parallelism between the molecular conductivities of acids and their heats of neutralization was the first proof of Arrhenius' hypothesis. He relied on thermochemistry and completed his dissertation. He presented his dissertation in June 1883 and published it in 1884 to obtain his doctorate. At that time, Wilhelm Ostwald was investigating the affinities of acids to bases, i.e. the intensity of the effects of acids on the rates of reactions they cause. He took the rate constants as a measure of the relative strength of the acids. After receiving Arrhenius' thesis, he measured the acid's molecular conductivities and found a remarkable proportionality to the reaction rate constants of the hydrolysis of methyl acetate and the inversion of cane sugar caused by them. This was the second proof of Arrhenius' hypothesis, based on the results of chemical kinetics. A memoir presented in 1885 by J. H. van 't Hoff on the analogy between the osmotic pressure of a highly dilute solution separated from the pure solvent by a

semipermeable membrane and the pressure of an ideal gas containing the same number of particles as the solution led to probably the most convincing proof of the Arrhenius hypothesis. This analogy corresponded to Avogadro's well-known law, which is  $PV=RT$ . He found that the pressure for non-conductors such as glucose followed this law, but was higher for electrolytes. This deviation was accounted for by the van 't Hoff factor  $i$ , which indicates into how many particles the solute – at least partially – has dissociated, so that the modified law is  $PV=iRT$ . The factor  $i$  could be deduced from Raoult's freezing point depression, and could also be calculated using Arrhenius' degree of dissociation  $\alpha$ . The degree of dissociation, in turn, was determined from the ratio of the conductivity of a dilute electrolyte solution and that under limiting conditions. The agreement found between the factors  $i$  determined by the two independent methods was the third proof of the Arrhenius hypothesis. There was a fourth proof, namely the additivity of physical properties. With these four nonelectrical and independent proofs, the 56 theses of Arrhenius' dissertation became the groundbreaking theory of *dissociation of substances dissolved in water*, which he published in 1887. In 1903 the Nobel Prize in Chemistry was awarded to him “in recognition of the extraordinary services he has rendered to the advancement of chemistry by his electrolytic theory of dissociation”.

**Keywords:** Dissociation Theory, Arrhenius, Electrolyte, Solution, Activity Coefficient.

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## INTRODUCTION

The 1880s, to which this article refers, were remarkable years, for in that decade the prevailing view that the molecules of electrolytes consist in their solutions of oppositely charged ions which are tightly bound together and can be separated only by an electric force acting on them was replaced by a radically different theory. This conventional view dated back nearly eight decades to the time of Theodor von Grotthuß and Humphry Davy. This view was challenged but by no means generally replaced by the free-ion hypothesis of Rudolf Clausius in 1857.<sup>[1-3]</sup> We have described its history in our earlier articles<sup>[4, 5]</sup> and do not repeat it here. Instead, we will focus on the pioneering theory of Svante Arrhenius.

Arrhenius' scientific interest was in the conductivity of highly dilute electrolyte solutions. This was the subject of his dissertation, which ultimately consisted of a collection of 56 theses or propositions. He presented his dissertation to the Royal Swedish Academy of Sciences in June 6, 1883, and published it in 1884.<sup>[6, 7]</sup> After a break of about three years, he published his theory of electrolyte dissociation in 1887.<sup>[8, 9]</sup>

Remarkably, Arrhenius managed to form his hypotheses into a solid theory by relying on results obtained by other scientists in the fields of non-electrical phenomena in physics and chemistry. In this article, the chronology of this successive confirmation of his theory is traced.

The historical overview, starting from a collection of 56 theses of a dissertation up to the groundbreaking theory “*Ueber die Dissociation der in Wasser gelösten Stoffe*”<sup>[8]</sup> (On the dissociation of substances dissolved in water) is the subject of the present article.

## SVANTE ARRHENIUS: BIOGRAPHY

Svante August Arrhenius, born in 1859 in Vik (also Wik or Wijk) near Uppsala, Swedish Kingdom, attended the cathedral school in Uppsala, matriculated in chemistry and mathematics at Uppsala University in 1876, graduating as early as 1878. His photo from that year is shown in Figure 1.

He then began studies of chemistry with lectures in mathematics and laboratory work in autumn of 1878 at the Swedish chemist, mineralogist and oceanographer Per Teodor Cleve, professor of chemistry from 1874 to 1905 at the University of Uppsala. Arrhenius, however, realized that his interests lay more in the overlapping area between physics and chemistry. Since the opportunities to work on such topics were not favorable at Uppsala University, he changed to the Physical Institute of the Swedish Academy of Sciences in Stockholm in 1881,



**Figure 1.** Photo of Svante Arrhenius from 1878, the year when he began his studies at the University in Uppsala. Provided by courtesy of the archives at the Royal Swedish Academy of Sciences.

where Erik Edlund (1819 – 1888), professor of physics, agreed to supervise him for his dissertation on the condition that he works independently and deals with topics of his own choosing.

Edlund had a very great diversity of interests from which Arrhenius profited considerably. Edlund explored, for example, electric sparks,<sup>[10, 11]</sup> atmospheric electricity and aurora borealis,<sup>[12]</sup> streaming potentials and dealt with theories of electrical phenomena.<sup>[13, 14]</sup>

After Arrhenius had initially tried to find a method for determining the molecular weight of chemical compounds in solution – albeit unsuccessfully and without knowledge of Raoult's paper from 1882<sup>[15]</sup> – a topic he had begun at Uppsala, and which he continued in Edlund's laboratory, he turned his interest to the electric conductivity of dilute electrolyte solutions.

#### *Arrhenius' first publication*

Most readers probably do not know that Arrhenius' very first publication was not his dissertation, but his own article published shortly before. In the spring of 1882 he had the opportunity to carry out independently in Edlund's physical laboratory a study of the polarization of electrodes, an undesirable effect of great importance in determining the resistances of electrolyte solutions. He measured the time course of the decrease in polarization current at the electrodes after the direct current had been switched off. From the results he derived some general conclusions which, however, need not be further discussed in the present context. Arrhenius paper "*Undersökning med Rheotom öfver den Galvaniska Polarisations Försvinnande i ett Polarisationskärl, hvars Plattor äro förbunda genom en metallisk Ledning*"<sup>[16]</sup> (Examination of the disappearance of galvanic polarization in a polarization vessel with a rheotome, the plates of which are connected by a metallic conductor) was dated October 11, 1882. It is probable that Arrhenius did not choose the subject of this study by chance, for knowledge of the operation of the device was of advantage for the measurements of the conductivities of dilute electrolyte solutions in his dissertation, which he began in the winter of 1882/1883, only a few weeks after the publication of this first paper.

#### THE DISSERTATION: RECHERCHES SUR LA CONDUCTIBILITÉ GALVANIQUE DES ÉLECTROLYTES

When in the winter of 1882/1883 Arrhenius began with a dissertation studying highly diluted solutions, he was faced with the unpleasant situation that only a few

publications had appeared on the subject up to that time, mainly those published by Friedrich Kohlrausch<sup>[17-25]</sup> and Rudolf Lenz.<sup>[26-29]</sup> Although Kohlrausch and Lenz had published reliable values for conductivities in recent years, they were of little help to Arrhenius. Kohlrausch reported comprehensive studies of the conductivities of a large number of dilute solutions from 1874 to 1879,<sup>[17-24, 30, 31]</sup> but their electrolyte concentrations were too high for Arrhenius' objective. They were usually greater than about 5% by weight and reached for some solutes nearly 100%. In 1878 Lenz did investigate solutions with lower molecular electrolyte concentrations in the range of  $10^{-2}$  equ.L<sup>-1</sup>, but his work was limited to the small group of potassium, sodium and ammonium salts and hydrogen acids.<sup>[28]</sup> Moreover, the concentration ranges were still too high for Arrhenius' purposes.

Arrhenius emphasized on pages 3 and 4 of his dissertation "*Recherches sur la conductibilité galvanique des électrolytes*"<sup>[6, 7]</sup> – the dissertation was written in French – that Kohlrausch had announced several times a work with conductivities in highly dilute solutions. But since this had not yet appeared – Kohlrausch's article "*Ueber das Leitungsvermögen einiger Electrolyte in äusserst verdünnter wässriger Lösung*" (On the conductivity of some electrolytes in extremely dilute aqueous solution) was not published until 1885<sup>[32]</sup> – Arrhenius decided to begin the investigation he had planned even without knowing Kohlrausch's results.

Arrhenius carried out the experimental part of his dissertation in Edlund's laboratory in Stockholm in the winter of 1882/1883 and spring of 1883. In May 1883 he wrote the second, theoretical part of his dissertation at his parents' home in Uppsala. Initially Arrhenius wrote his dissertation in one part, but it was rather complicated to read and somewhat confusingly structured. Sven Otto Pettersson, then docent of physics in Uppsala, who was asked by Arrhenius to read the dissertation in advance, found the work worthy of submission, but advised Arrhenius to restructure it; so Arrhenius divided it into two parts. He also recommended to avoid the term *dissociation*, since it was understood to mean the decomposition of a compound into its smaller constituents under the influence of heat.

According to Pettersson's advice Arrhenius divided the initial version into Part 1<sup>[6]</sup> which consisted from 63 pages, and into Part 2<sup>[7]</sup> with 89 pages.

It may be confusing that Arrhenius did never use the term *dissociation* in his dissertation. *Dissociation* for thermal decomposition was introduced in 1857 by the French chemist Henri Étienne Sainte-Claire Deville (1818 – 1881) in his paper "*Sur la dissociation ou la décomposition spontanée des corps sous l'influence de la*

*chaleur*” (On the spontaneous dissociation or decomposition of bodies under the influence of heat).<sup>[33]</sup> Examples are the decomposition of ammonium chloride on heating into *HCl* and *NH<sub>3</sub>*, or of molecular iodine *J<sub>2</sub>* into its atoms, and the reversible recombination of the gaseous particles to the parent molecules on cooling. Pettersson foresaw that the term dissociation for the cleavage of electrolyte molecules in solutions would meet with disapproval from the chemistry professors at the university. Therefore, Arrhenius used in his dissertation the terms electrically *active* and *inactive* for the ionic and the non-ionic particles.

We emphasize that we rely on the two-part dissertation submitted to the Royal Swedish Academy of Sciences in June 1883 and published in 1884.<sup>[6, 7]</sup>

PREMIÈRE PARTIE. LA CONDUCTIBILITÉ DES SOLUTIONS AQUEUSES EXTREMEMENT DILUÉES DÉTERMINÉE AU MOYEN DU DÉPOLARISATEUR

In Part 1, “The Conductivity of Extremely Dilute Aqueous Solutions Determined by Means of the Depolarizer”,<sup>[6]</sup> Arrhenius first described in detail the apparatus and the devices, the experimental conditions and the chemicals.<sup>1</sup> He paid special attention to the control of the correct function of the “*depolarisateur*” Edlund had constructed,<sup>[34]</sup> and by which he could transform constant into sinusoidal alternating current.<sup>2</sup> It is schematically depicted in Fig. 3 of Arrhenius’ dissertation<sup>[6]</sup>, and explained there and in Edlund’s paper from 1875.<sup>[34]</sup>

<sup>1</sup> We give here a more detailed description of his experimental conditions, because Arrhenius performed his experiments in a very contrarian manner compared to Kohlrausch, who measured the conductivities in about the same years. In part 3 of our series, we described how much importance Kohlrausch attached to measuring values that were as accurate as possible. He then derived empirical laws from them. Arrhenius, on the other hand, as he himself said, was satisfied with less accurate values. He was, however, able to recognize in them an existing tendency from which he deduced his hypotheses.

<sup>2</sup> Edlund’s depolarizer, incidentally, was severely criticized by E. Dorn,<sup>[35]</sup> <sup>[36]</sup> but his criticism was rejected by Edlund.<sup>[37]</sup> It is, however, remarkable that even in 1886, two years after the completion of Arrhenius’ dissertation the problem of measuring accurate conductivities with alternating current was still a matter of question, at least for Oliver Lodge, to whom we will return below. He added a critical comment in ref. <sup>[38]</sup>, footnote 1 on p. 384 in “*Translation of a letter received from Dr. Arrhenius respecting the above Criticism*” which read: “*This opens a large question, viz., how far it is advisable to depend on the use of alternating currents as a device for avoiding polarisation difficulties .... Unless the question of electro-chemical capacity be thus considered, and either eliminated by calculation or proved to be negligible by experiment, the presumed advantage of alternating currents in dealing with electrolytic resistance is illusory.*” Nowadays, *depolarizer* is the obsolete synonym for an electro-active substance (see IUPAC, <https://doi.org/10.1351/goldbook.D01599>, *Compendium of Chemical Terminology, 2nd ed. (the “Gold Book”)*).

The measuring cell which Arrhenius used is shown in Figure 2. It served for both, the preparation of the different dilute samples and the measurement of their resistances in a rather unconventional, but economical manner.

The measurement procedure was as follows. First, a weighed amount of electrolyte was placed in the glass vessel where it was dissolved in 35 cm<sup>3</sup> distilled water. The quantity of water and therefore the concentration of the electrolyte were determined by weighing the vessel before and after filling. After measuring the resistance, part of the solution was removed and replaced by distilled water, and the two liquids were mixed directly in the vessel. The dilution was determined again by weighing the vessel after replacing a part of the solution and after refilling with solvent. This procedure was carried out several times in succession, preparing solutions with three to six different concentrations, usually four to five. Solutions were diluted till the measured resistance approached that of pure water (in fact, the lowest concentration Arrhenius measured was in the range of about 10<sup>-4</sup> normal.<sup>3</sup>)

The resistances of the dilute electrolyte solutions were between several hundred and about 120000 Ohm. The reproducibility was of the order of 1% or less. However, the chosen procedure had the disadvantage that the concentrations were not determined by quantitative analysis and were therefore of low accuracy, which consequently affected the molecular conductivities, a systematic error that Arrhenius readily accepted.<sup>4</sup>

Arrhenius measured the electrical resistances of 47 compounds, i.e. salts, bases, and acids at various dilutions<sup>5</sup>, and from these their molecular conductivities<sup>6</sup>. He found that the conductivity in dilute solutions

<sup>3</sup> Arrhenius often used the term “normal” as a measure of the concentration. It was introduced by Karl Friedrich Mohr in 1855 in his textbook about titrimetric analysis.<sup>[39]</sup>

<sup>4</sup> Arrhenius pointed out this low accuracy in § 13. *Conductibilité moléculaire*. p. 38. “From formula (3), the molecular conductivity can be calculated in each special case. The named formula contains the amount of dissolved electrolyte (P). It was not possible to determine this quantity analytically, but only by weighing the electrolytes. As the substances examined are hygroscopic and also somewhat impure, this determination cannot possess great accuracy.” In his reply from 1886 to Oliver Lodge’s criticism on his low accuracy (ref. <sup>[38]</sup>, p. 386), he wrote: “6. That the last work of Kohlrausch contains as you say incomparably better experimental data (especially more accurate) is true enough. But without my data I could not have formed a coherent picture of the whole.”

<sup>5</sup> The apparent paradox that the conductivity of an electrolyte solution decreases with increasing dilution, but its molecular conductivity increases, has already been clarified in our previous article<sup>[5]</sup> in connection with Kohlrausch’s law of independent ion migration.

<sup>6</sup> The molecular conductivity *k/m* is the ratio of the specific conductivity, *k*, and *m*, the concentration of the solution in g.equiv. per liter. It is the equivalent conductivity, as Rudolf Lenz emphasized in his study of

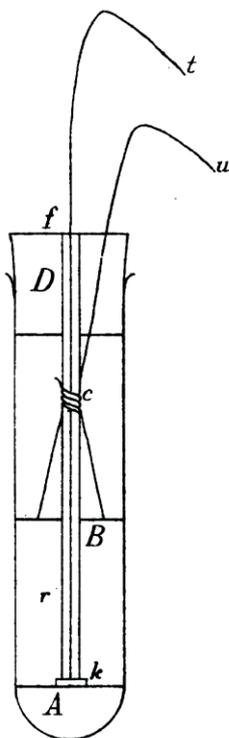


Fig. 4.

**Figure 2.** Scheme of the cell Arrhenius used for the measurement of the resistance. Glass vessel, height, ca. 150 mm; diameter, 25 mm. A, B: platinized platinum electrodes, 2/7 mm thickness. Lower electrode A welded to a thick platinum wire, fused into a narrow glass tube K, which passed through the center of the conical cork or rubber plug D, attached to tube r at the top at f. Upper electrode B: perforated in center to allow tube r to pass through. Two long platinum wires, riveted to plate B, attached to the tube at point c. One of these wires formed with t one of the poles. k, small rubber plate to hermetically seal vessel at the bottom. The test liquid (30 to 40 cm<sup>3</sup>) filled the vessel to a point slightly above B. Reproduced from Fig. 4 of Arrhenius' dissertation.<sup>[6]</sup>

for most electrolytes is proportional to the number of electrolyte molecules. If this is not the case, it must be assumed that chemical reactions take place upon dilution, but he had no conclusive explanation at first. Yet it was these effects that attracted his particular interest in his work.

Arrhenius introduced a quantity he called "dilution exponent" and measured its dependence on the dilution for a given electrolyte. The dilution exponent was the ratio by which the resistance of a salt solution increases when it is diluted by water to twice its volume. In the best case, the exponent is 2.<sup>7</sup>

haloid compounds in 1877.<sup>[26]</sup>

<sup>7</sup> To be precise: As Arrhenius measured and tabulated resistances, he

In § 13. he calculated the molecular conductivities, actually the conductivity at an electrolyte concentration in equivalent per liter of solution, as function of the concentration in the series of dilutions prepared from one and the same electrolyte solution. He found from his own data, and from those he has taken from publications of Kohlrausch<sup>[23, 24]</sup> und Lenz,<sup>[28]</sup> that the molecular conductivity increases with increasing dilution for all 47 electrolytes he investigated (in the summary of Part 1 he mentioned only 45 electrolytes). The electrolytes were salts, and only five bases and acids<sup>8</sup> each. Their molecular conductivity approached a certain limiting value; the same result found Kohlrausch.<sup>[23]</sup> For most electrolytes, especially for simple ones like the alkali halogenides, molecular conductivity increased slightly and linearly with increasing dilution. However, some solutes, especially ammonia and acetic acid, exhibited deviating properties. Their conductivity remained at low values at lower dilution, but abruptly increased when dilution increased. We have discussed these effects already in Part 3 of our series;<sup>[5]</sup> see the lower part of Figure 5 there. The complete plot was published by Kohlrausch in 1885.<sup>[32]</sup>

To find an explanation for this deviating shape of the curves, Arrhenius resorted to Hittorf's observation of the formation of complex salts of cadmium and iodine.<sup>[40]</sup> He stated on p. 60 in *Thesis 11*. (the entire dissertation comprised 23 paragraphs and 56 theses, in French "*propositions*"): "Aqueous solutions of all electrolytes contain the dissolved electrolyte at least in the form of molecular complexes", and attributed the observed irregularities to possible chemical decomposition of complex molecules with increasing dilution.

He postulated in *Thesis 2*: "If two or more salts are dissolved in the same non-conducting solvent, the conductivity of the solution is equal to the sum of the conductivities which the solution would possess if only one salt were dissolved at one time and the other salt alone at another time." In § 16. *Chemical action*, he formulated the following important two theses:

*Thesis 4.* If, when diluting any solution, the conductivity does not change in proportion to the amount of electro-

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defined the dilution exponent as the ratio by which the resistance increases when a given electrolyte solution of the series is diluted. It is obvious that this indicates the corresponding decrease in conductivity. If the solution is diluted exactly to twice its volume, the dilution exponent should be 2, because the number of the initial conducting molecules is exactly bisected. Arrhenius found that most electrolytes had values of 1.95 to 2, but some deviated with higher, others with lower values.

<sup>8</sup> Arrhenius measured the resistances of hydrochloric, nitric, sulphuric, phosphoric and boric acid.

lyte, a chemical change must have occurred in the solution due to the addition of the solvent.

*Thesis 5.* If two substances are dissolved in water at the same time and thesis 2. is not applicable, a chemical process must have taken place between the two.

In § 17. he discussed the peculiarities of hydrates,<sup>9</sup> and in § 20. the nature of the resistance of electrolytes. He attributed the large conductivity of acids to the fact that they have hydrogen as a cation which, because of its small molecular volume, penetrates most easily into the solvent.

In the last chapter, § 21: *Properties of solutions of normal salts*, he makes a whole series of conjectures and speculations. The most important hypotheses, however, relate again to the decay of complex molecules, such as those of Hittorf quoted above. He argued in *Theses 11, 12 and 13* that complexes probably decay upon the addition of solvents, so that the complexity approaches asymptotically a lower limit. From this follows the important hypothesis that the more completely complexes decay, the more molecular conductivity increases. Important for the further development of his theory is his conviction (p. 60, 61)

*Thesis 11.* Aqueous solutions of all electrolytes contain the dissolved electrolyte, at least in part, in the form of molecular complexes.

*Thesis 12.* The limit, to which the complexity of a normal salt dissolved at extreme dilution tends to approach, is of the same degree for all normal salts. (Probably this thesis applies for all electrolytes.)

*Thesis 13.* It is likely that this limit is reached only when the salts are divided into simple molecules as represented by the chemical molecular formula.

From today's perspective, this could be seen as a pre-stage to his dissociation theory, as it transfers the idea of the decay of molecular complexes into individual molecules to the decay of molecules into their ions. However, the remaining problem was why the molecular conductivities of most electrolytes regularly increase with increasing dilution, and why some of them increase in deviating manner.

<sup>9</sup> By hydrates Arrhenius meant acids and bases, using the prevailing term for them. The theory of hydrates of compounds, not necessarily only of electrolytes, will be the motive of a vigorous rejection of Arrhenius' theory of dissociation of electrolytes right after its publication. This earlier hydrate theory should not be confused with the modern theory of solvation or hydration of charged particles. This interesting chapter on this controversy, usually not even mentioned in textbooks and therefore widely unknown, will be covered in a future part of our review series.

## SECONDE PARTIE. THÉORIE CHIMIQUE DES ÉLECTROLYTES

Part 2, "Chemical Theory of Electrolytes"<sup>[7]</sup> of Arrhenius' dissertation began in §1 with his considerations of "Ammonia as Electrolyte". It was well known by him that compounds such as liquid, pure and anhydrous ammonia – its boiling point is  $-33^{\circ}\text{C}$  -do not transport electricity, but they become conductors when water is added. In Volume II. p. 147, of Marcellin Berthelot's<sup>10</sup> *Mécanique chimique*, § 2. *Dissolution des gaz*,<sup>[51]</sup> he found

*Par exemple, la solution du gaz ammoniac, saturée à basse température se trouve contenir l'eau et le gaz suivant des proportions définies: soit  $\text{AzH}^3 + \text{H}^2\text{O}^2$ , très sensiblement. Cet hydrate cristallise d'ailleurs dans un mélange réfrigérant.* (For example, the solution of ammonia gas, saturated at low temperature, contains water and gas in defined proportions: i.e.  $\text{AzH}^3 + \text{H}^2\text{O}^2$ , very substantially. This hydrate crystallizes in a refrigerant mixture.) [Symbol Az stands for French *azote*, i.e., nitrogen. Author's note].

Since, according to the prevailing hydrate theory, hydrates were generally assumed to be dissolved in the same composition in which they crystallize from their solution, Arrhenius thus had every reason to believe that ammonia hydrates exist at least partially in solution as  $\text{AzH}_4\text{OH}$ . Berthelot further wrote

*Mais tous ces composés sont peu stables, et susceptibles de subsister seulement en présence des produits de leur décomposition; c'est-à-dire que le gaz dissous  $[\text{H}_3\text{Az}]$ , le liquide dissolvant et leur combinaison forment un système en équilibre, équilibre dont les conditions varient avec la température et la pression.* (But all these compounds are not very stable, and likely to remain only in the presence of the products of their decomposition; that is to say, the dissolved gas, the dissolving liquid and their combination form a system in equilibrium, an equilibrium whose conditions vary with temperature and pressure.)

This means that the equilibrium  $\text{NH}_3 + \text{H}_2\text{O} = \text{NH}_4\text{OH}$  is established. From these three components water and ammonia are non-electrolytes, only the weak

<sup>10</sup> Marcellin Pierre Eugène Berthelot (1827 – 1907) was the most influential and respected chemist in France in his time. He was famous for his innovations in many scientific areas, among others in organic synthesis,<sup>[41],[42],[43]</sup> and in biochemistry and pharmacology. He introduced thermochemistry, where he coined the terms exothermic and endothermic, before thermodynamics took over the dominant role. His standard books about thermochemistry (e.g. refs. <sup>[44],[45],[46]</sup>) with numerous data were used by Arrhenius to support his theory. Since mid 1880 Berthelot's interest turned to the history and philosophy of sciences,<sup>[47]</sup> in particular to alchemy.<sup>[48],[49],[50]</sup>

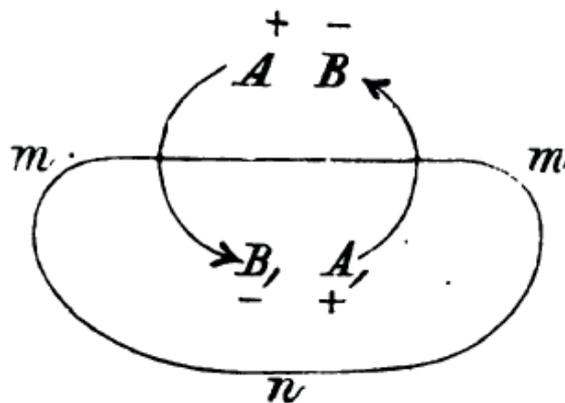
base  $NH_4OH$  has the capability to contribute to electric conductivity by splitting off the cation  $NH_4^+$  and the anion  $OH^-$ . According to the law of mass action, the equilibrium shifts towards  $NH_4OH$  when water is added, which is reflected in *Thesis 14*. “The conductivity of an ammonia solution is caused by a small amount of  $AzH_4OH$ , which is contained in it and which increases with the dilution of the solution.”

Kohlrausch observed the same effect upon dilution of acetic acid we have already mentioned above, and an analogue relation between conductivity and dilution with other acids he had investigated.<sup>[21]</sup> Based on these facts Arrhenius came to the main conclusion that the amount of the conducting part of the electrolyte increases with dilution at the expense of the non-conducting part, and formulated one of the most important theses of his dissertation, which turned out to be the nucleus of his later dissociation theory. Literally it reads (and stated that *Thesis 15*, also applies to bases).

*Thesis 15. La solution aqueuse d'un hydrate quelconque se compose, hors l'eau, de deux parties, l'une active (électrolytique), l'autre inactive (non-électrolytique). Ces trois parties constituantes, l'eau, l'hydrate actif, et l'hydrate inactif, forment un équilibre chimique, tel qu'à une dilution la partie active augmente et la partie inactive diminue. (L'activité électrolytique se confond avec l'activité chimique). (The aqueous solution of any hydrate is composed, apart from water, of two parts, one active (electrolytic), the other inactive (non-electrolytic). These three constituent parts, water, active hydrate, and inactive hydrate, form a chemical equilibrium, such that on dilution the active part increases and the inactive part decreases.) (The electrolytic activity is equal to the chemical activity).*

Then Arrhenius introduced the term “activity coefficient”<sup>11</sup> and defined it as

*Le coefficient d'activité d'un électrolyte est le nombre exprimant le rapport du nombre d'ions qu'il y a réellement dans l'électrolyte, au nombre d'ions qui y seraient renfermés, si l'électrolyte était totalement transformé en molécules électrolytiques simples. (Ces molécules sont nécessairement constituées d'une manière analogue à celle des sels.) (The activity coefficient of an electrolyte is the number that expresses the ratio of the number of ions that are present in the electrolyte to the number of ions that would be present if the electrolyte were totally transformed into simple electrolytic molecules. (These molecules are necessarily constituted in a manner similar to that of salts.)*



**Figure 3.** Schematic drawing of the flow of the circular current. For explanation, see main text.

In § 3. *Hypothesis of Clausius and Williamson*, Arrhenius addressed the question of the number of free dissociated ions in a dilute electrolyte solution, resorting to the free-ion hypothesis of Clausius. Arrhenius tried to draw conclusions from this hypothesis, which are exemplified in Figure 3. Although this figure was used for a different conclusion, it is fully suitable for the present one.

In this figure, two molecules of the same electrolyte are shown (we negate the curve labeled  $mm,n$ ). The upper molecule consists of cation  $A$  and anion  $B$ , the other one of  $A_1$  and  $B_1$ . All ions are charged with the same amount of electricity. Cation  $A_1$ , for example, can split off and combine with anion  $B$  of the next molecule. As a result, cation  $A$  is released and can unite with anion  $B_1$ . In solutions, of course, not only these two molecules, but any larger number  $A_2B_2$ ,  $A_3B_3$ , ...  $A_nB_n$  ... are present, so that this process extends over several molecules. However, it will not end until the cation of the last molecule has united with the anion of the first.

Though Arrhenius believed that this process was very fast, there were still free ions existing for short time during this exchange. These have moved in a closed loop, as well as the electricity charged with them. This transport of electricity was called by Arrhenius a *circular current*. It is the natural state of electrolyte ions in a solution – mind you – without an applied electric potential, that is, under the condition that no current flows through the solution. This means that circulating currents occur permanently in an electrolyte solution.

Because of its connection with the circular flows just discussed, § 6 shall now be treated prior to § 4. However, before continuing with this paragraph, we point out that this concept of the circular current was already introduced by Grotthuß as early as 1819 who called it *infinite circular molecular exchange*, but was hardly taken note of.

<sup>11</sup> It is equal to the *dissociation ratio* Oliver Lodge defined in 1885 on p. 756 of ref. <sup>[52]</sup> for dissociated molecules in solutions.

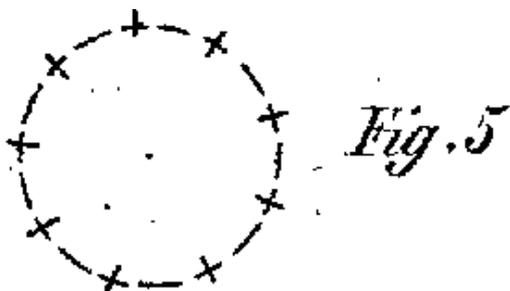
Although an excerpt of Grotthuß' work appeared in Gilbert's *Annalen der Physik*,<sup>[53]</sup> his entire work was published in the scarcely accessible *Annalen der Curländischen Gesellschaft für Litteratur und Kunst*.

Grotthuß wrote in his article in reference to Figure 5, shown below as Figure 4

*“In den Flüssigkeiten, die aus heterogenen Elementartheilchen bestehen, ....., muss zwischen diesen Elementartheilchen ein beständiger Galvanismus, und dadurch ein beständiger wechselseitiger polarischer Molekularaustausch unterhalten werden, den man durch das auf Taf. III in Fig. 5 dargestellte kreisförmige Schema ausdrücken kann. Jede Wasserzersetzung, die man mit dem Namen chemische belegt, ist daher nur eine Störung des fortwährenden Molekulargalvanismus, oder eine Ausglei chung des unendlichen kreisförmigen Molekularaustausches zu einem endlichen linienförmigen.“* (In liquids consisting of heterogeneous elementary particles ..... a constant galvanism must be maintained between these elementary particles, and thus a constant mutual polaric molecular exchange, which can be expressed by the circular scheme shown on Plate III in Fig. 5. Any water decomposition, which is called chemical, is therefore only a disturbance of the continuous molecular galvanism, or a leveling of the infinite circular molecular exchange to a finite linear one.)

After this retrospect to the unexpectedly early concept of the *infinite circular molecular exchange* by Grotthuß, which resembles also Williamson's 1850 hypothesis<sup>[54]</sup> on the permanent exchange of “radicles” between molecules by double decomposition we continue with § 6. It addressed Arrhenius' conclusion about the consequences of this current when a second electrolyte, *CD*, is dissolved in the solution instead of a single electrolyte, e.g., *AB* as described above.

§ 6. *The double decomposition.* If *AB* and *CD* move through the inactive solvent by the circular current,



**Figure 4.** Circular current in a liquid which consists of positively and negatively charged particles. Grotthuß did not call them ions in his text, because this term was unknown in his time. Note that no electric potential is applied, and therefore no current flows through the liquid. Taken from ref. <sup>[53]</sup>.

again without being driven by an applied electric force, consequently the pairs *AD* and *CB* also form from *AB* and *CD* by double decomposition. Thus, all four electrolytes are present in the solution at the same time. Their amounts depend on the respective activity coefficients of the electrolytes (the present degree of dissociation). If these are equal, the amounts of all four substances are also equal. If initially one equivalent each of *AB* and *CD* are dissolved, half an equivalent of each of the four electrolytes *AB*, *CD*, *AD* and *CB* will be found at equilibrium. For unequal affinity coefficients, a corresponding equilibrium is reached by double decomposition, and *Thesis 29* applies: “Every salt dissolved in water partially decomposes into acid and base. The amount of these decomposition products is the more substantial the weaker the acid and the base are and the greater the amount of water is.” This thesis leads inevitably to the chief question of the strength of acids and bases.

Kohlrausch differentiated two groups of acids (the same applied for bases). Strong acids show a linear dependence of the molecular conductivity on the number of dissolved molecules, weak acids do not. For both groups some examples of the molecular conductivity,  $\lambda$ , are listed in Table 1.

It should be recalled that Arrhenius had previously equated the molecular conductivity with the activity coefficient. Considering the molecular conductivities of the acids and bases from Table 1, he formulated *Thesis 33*. “The greater the activity coefficient (molecular conductivity) of an acid, the stronger it is. This thesis also applies to bases”.

With this thesis he indirectly formulated his acid-base theory. It stated that acids are compounds that dissociate into  $H^+$  ions and negatively charged anions in an aqueous solution. Analogously, bases dissociate in water to  $OH^-$  ions and to cations. Remarkably, he did not define it literally at any point in his dissertation, but it can be clearly understood as such because of the multiple mentions of the active parts of acids and bases.

The values of the molecular conductivities in Table 1 indicate that the hydrohalic and nitric are strong acids, acetic acid is weak, boric acid is the weakest. In the group of the bases, sodium and potassium hydroxide are strong, ammonium hydroxide is a weak base.<sup>12</sup>

Arrhenius, however, was not satisfied with the fact that the ranking of the strength was based only on the conductivity, and wanted to evaluate it by an independent method which was not based on electric

<sup>12</sup> Water is a special case, it has the lowest conductivity of all compounds; it is listed in the group of acids, but it as was generally known that it can also act as a base.

**Table 1.** Molecular conductivities,  $\lambda$ , of strong (Group I) and weak (Group II) acids and bases. Concentrations of electrolyte solutions: 1 g equiv. solute per liter solution. The conductivities were taken or calculated from ref. [21], that of distilled water see Première partie, § 8.<sup>[6]</sup> The table is reproduced from Arrhenius' dissertation, Seconde partie,<sup>[7]</sup> p. 14 and 15.

<b>Groupe I.</b>	
Acide chlorhydrique ( <i>HCl</i> )	$\lambda = 284 \cdot 10^{-7}$ .
» bromhydrique ( <i>HBr</i> )	$278 \cdot 10^{-7}$ .
» iodhydrique ( <i>IJ</i> )	$298 \cdot 10^{-7}$ .
» azotique ( <i>HAzO<sub>3</sub></i> )	$296 \cdot 10^{-7}$ .
» sulfurique ( $\frac{1}{2}H_2SO_4$ )	$192 \cdot 10^{-7}$ .
» oxalique ( $\frac{1}{2}H_2C_2O_4$ )	$57,1 \cdot 10^{-7}$ .
» phosphorique ( $\frac{1}{3}H_3PO_4$ )	$20 \cdot 10^{-7}$ .
<b>Groupe II.</b>	
Acide tartrique ( $\frac{1}{2}C_4H_6O_6$ )	$6,9 \cdot 10^{-7}$ .
» acétique ( <i>CH<sub>3</sub>COOH</i> )	$1,26 \cdot 10^{-7}$ .
» borique ( $\frac{1}{3}H_3O_3B$ )	$0,044 \cdot 10^{-7}$ <sup>2)</sup> .
Eau distillée la plus pure ( <i>HOH</i> )	$< 0,000013 \cdot 10^{-7}$ <sup>2)</sup> .
<b>Groupe I,</b>	
Potasse caustique ( <i>KOH</i> )	$\lambda = 172 \cdot 10^{-7}$ .
» » ( <i>NaOH</i> )	$149 \cdot 10^{-7}$ .
Eau de baryte ( $\frac{1}{2}BaO_2H_2$ )	$137 \cdot 10^{-7}$ <sup>3)</sup> .
» » chaux ( $\frac{1}{2}CaO_2H_2$ )	$134 \cdot 10^{-7}$ <sup>3)</sup> .
Hydrate de lithium ( <i>LiOH</i> )	$125 \cdot 10^{-7}$ .
<b>Groupe II.</b>	
Ammoniaque caustique ( <i>H<sub>4</sub>AzOH</i> )	$0,84 \cdot 10^{-7}$ .

properties. In his Nobel Lecture, held December 11, 1903 on “*Development of the theory of electrolytic dissociation*”<sup>[55]</sup> he admitted that he himself felt that a single line of evidence was not sufficient for a well-founded theory. He said

“If this concept had only been applicable to accounting for the phenomenon of electrical conductivity, its value would not have been particularly great.”

“An examination of the numerical values adduced by Kohlrausch and others for the electrical conductivity of acids and bases as compared with Berthelot's and Thomson's measurements of their relative strengths in terms of their chemical effect showed me that the acids and bases with the greatest conductivity are also the strongest. I was thus led to the assumption that the electrically active molecules are also chemically active, and that conversely the electrically inactive molecules are also chemically inactive, relatively speaking at least. *etc.*”

For the sake of completeness, we think it appropriate to include a chapter, albeit brief, on thermochemistry, which, incidentally, was later replaced by the emerging field of thermodynamics.

## 1ST PROOF. THERMOCHEMISTRY, HEAT OF NEUTRALIZATION

Thermochemistry, a branch of physical chemistry, deals with the exchange of heat energy at changes of state of a chemical system, e.g., at phase transformations and chemical reactions. It hypothesizes that all chemical changes involve the generation of heat, that the heats of reaction were direct measures of the chemical affinity, and that those processes take place where the most heat is generated. Such processes are dissolving, mixing, diluting of substances, the decomposition and recombination of compounds, the decomposition of salts by acids, the determination of the stoichiometry of acids and bases, the reaction of acids with bases, i.e., neutralization reactions, the change of the aggregate state such as melting or evaporation, etc.

Thermochemical experiments were first described 1838 in a paper from the estate of Pierre Louis Dulong (1785 – 1838),<sup>[56]</sup> followed by the comprehensive “*Thermo-chemische Untersuchungen*” (Thermochemical studies) by Germain Henri Hess<sup>13</sup> from 1840 to 1842,<sup>[57-65]</sup> and between 1844 and 1850 by the investigation of Abria,<sup>[66]</sup> by Pierre Antoine Favre (1813 – 1880) and Johann Theobald Silberman (1806 – 1865),<sup>[67, 68]</sup> and by Thomas Andrews (1813 – 1885).<sup>[69-72]</sup>

However, the main contributions to the recent theory were published by the Danish chemist Hans Peter Jørgen Julius Thomsen<sup>14</sup> as early as 1853 and 1854 in four papers on “*Die Grundzüge eines thermo-chemischen Systems*” (The principles of a thermo-chemical system) in Poggendorff's *Annalen der Physik und Chemie*.<sup>[73-76]</sup> Nevertheless, the French chemist Marcellin Berthelot quoted above, who did not formulate a slightly modified form until 1865 as a lecture (in lessons at the Collège de France in 1865 and published it the same year in the *Revue des cours scientifiques*, see also ref. <sup>[77]</sup>) and also not until 1869 as a journal article in *Annales de chimie et de physique*<sup>[77]</sup> claimed the priority of thermochemistry, which led to a lifelong fierce controversy between the two scientists.

After a hiatus of fifteen years, Thomsen continued from 1869 to 1871 with extended studies on “*Wärmetönung*” (“heat toning”), as he called it, that is, the heat released or absorbed by the change of state of a sys-

<sup>13</sup> Hess formulated the law named after him,<sup>[57]</sup> also known the law of constant heat summation. It states that *the heat evolved or absorbed in a chemical process is the same whether the process takes place in one or in several steps.*

<sup>14</sup> Hans Peter Jørgen Julius Thomsen (1826 – 1909) was professor for chemistry at the University of Copenhagen from 1866 till 1891, and from 1883 till 1902 director of the *Polytekniske Lærestalt*, the later Danish Technical University.

tem. Of all the heats of reaction measured by Thomsen, Arrhenius was most interested in the heat of neutralization of an acid with a strong base in order to classify acids according to their strength on the basis of the amounts of heat they released. Between 1869 and 1870 Thomsen published a series of six paper on “*Thermochemische Untersuchungen*”<sup>[78-83]</sup> (Thermochemical studies) with heats of reaction of numerous acids, including those of neutralization. He collected the results from 1100 calorimetric experiments and 600 chemical reactions in “*Thermochemische Untersuchungen. I. Neutralisation und verwandte Phänomene*” from 1882.<sup>[84]</sup> It was the first volume of a series of four.<sup>15</sup> Cutouts from the tables with the values of monobasic hydrochloric, acetic and hydrocyanic acid which he published in 1869<sup>[79]</sup> and 1870<sup>[82]</sup> in *Annalen der Physik und Chemie* are shown in the upper panel of Table 2.

The main source Arrhenius quoted in his work was Marcellin Berthelot's 1879 book “*Essai de mécanique chimique fondée sur la thermochemie*.” Tabulated values of the heat of neutralization from *Tome I. Calorimétrie*,<sup>[44]</sup> *Livre III (Données numériques), Chapitre VI (Chaleurs de formation des sels)*, p. 383 ff., are shown in the lower panel of Table 2. These rounded values were taken by Arrhenius in his dissertation in Part 2, p.68.

In his dissertation Arrhenius discussed the reasons for the greater heat of neutralization of the strong acids and the lower heat of the weaker acids. He formulated the principle in § 20, p. 67, of Part 2. It read

§ 20. *Dégagement de chaleur aux reactions chimiques.*

“As we know, Mr. THOMSEN claims that all bases, when in the form of dissolved hydrates, release the same amount of heat by neutralizing the same amount of an acid. This simple fact is called “saline thermoneutrality”. In contrast, not all acids release the same amount of heat when they combine with a base. This fact seemed very bizarre to the savants of thermochemistry. However, according to the above, it seems easy to explain it. It is obvious that from the thermochemical point of view, two hydrates can be equal only when they are both in the *active state*. In the inactive state, the analogous compounds do not play the role of hydrates (acids or bases),

<sup>15</sup> Thomsen's motivation to publish this series from 1882 and 1886<sup>[84],[85],[86],[87]</sup> was due to reasons of priority. In the Introduction of the first volume in 1882 (p. 12, ref. <sup>[84]</sup>) Thomsen wrote “*Schon im Jahre 1853-54 hatte ich in den Annalen der Physik und Chemie, Bd. 88, 90, 91 und 92 [73],[74],[75],[76] die fundamentalen dynamischen Gesetze der chemischen Prozesse entwickelt. Da man aber mir die Priorität hierfür hat streitig machen wollen, werde ich im Folgenden einige Hauptpunkte dieser Abhandlungen wieder hervorheben.*” (Already in 1853-54 I had developed the fundamental dynamical laws of chemical processes in *Annalen der Physik und Chemie*, vol. 88, 90, 91, and 92. Since, however, one has wanted to dispute my priority for this, I will again emphasize some main points of these treatises in the following.)

**Table 2.** Heats of neutralization for different acids and bases. Upper panel: Thomsen's values from 1869 and 1870 for the monobasic hydrochloric, hydrocyanic and acetic acid. T; temperature in °C.  $\alpha$ ; number of equivalent base added to 1 equivalent acid. Concentrations: varying, typically 1 eq. in 200 or 400 L water. Taken from refs. <sup>[79, 82]</sup>. Lower panel: Table from Berthelot's 1879 book which was reproduced by Arrhenius in his dissertation, Part 2, p. 68.<sup>1</sup> Temperature 15°C. Numbers are in kcal. For details, see main text.

(Na Aq, H Cl Aq)									
No.	$\alpha = b$	T	$t_a$	$t_b$	$t_c$	r	s	pro Aeq.	
14	450	18,1	18,610	18,222	22,169	3438°	}	1/4	13740°
15		18,0	18,500	18,150	22,070	3430			
16		17,7	18,378	17,910	21,896	3438			
(Na Aq, H Cy Aq)									
55	450	16,9	17,690	17,025	18,110	697	}	1/4	2766
		17,5	17,740	17,120	18,170	686			
Q									
		$\alpha$	(Na Aq, $\alpha$ Q Aq)			(Na Aq, Q Aq)			
Essigsäure		}	1/2	6585°			6616°		
			1	13155			13155		
			2	13233			13170		

*Chaleurs de formation de quelques sels en dissolutions étendues d'après MM. BERTHELOT et THOMSEN.*

	HCl <sup>1)</sup>	HAzO <sub>2</sub>	HOOC <sup>1)</sup> HO	HOOC	1/2(COOH) <sup>1)</sup>	1/2H <sub>2</sub> SO <sub>4</sub>	1/2HSH	HOAz	1/2O <sub>2</sub>
NaOH.....	13,7	13,7	13,8	13,4	14,3	15,85	3,85	2,9	10,2
KOH.....	13,7	13,8	13,8	13,4	14,3	15,7	3,86	3,0	10,1
AzH <sub>3</sub> .....	12,45	12,5	12,0	11,9	12,7	14,5	3,1	1,8	5,8
1/2Ca(OH) <sub>2</sub>	14,0	13,9	13,4	13,5	18,5	15,6	3,9	—	9,8
1/2Ba(OH) <sub>2</sub>	13,85	13,9	13,4	13,5	16,7	18,4	—	—	11,1
1/2Sr(OH) <sub>2</sub>	14,1	13,9	13,8	13,5	17,6	15,4	—	—	10,5

<sup>1</sup> Berthelot's values in the lower table are rounded; Thomsen had given accurate values, for example, 2770 cal for HCN. These differences were insignificant for the ranking of the acids according to their strengths. Moreover, the heat of neutralization depends on the temperature.<sup>[79]</sup>

since they cannot unite with another type of hydrate of opposite sign and form water and salt. So, instead of assuming with THOMSEN that the hydrates are in “dissolved state”, we assume that they are in “active” state. Then we express the following, very plausible hypothesis: *Le procédé chimique à cause duquel un système d'un équivalent l'acide (actif) et d'un équivalent de base (aussi active) se transforme en un nouveau système, consistant d'un sel (non compliqué) et de l'eau, est accompagné d'un même dégagement de chaleur indépendant de la nature des hydrates.* (The chemical process of converting a system consisting of one equivalent of an (active) acid and one equivalent of a (also active) base into a new system consisting of a (non-complex) salt and water is accompanied by the same heat evolution, which is independent of the nature of the hydrates).

Arrhenius then described the sequence in which the neutralization reactions occurs: 1. Neutralization through the active parts of the hydrates. 2. New formation of active from inactive parts. 3. Neutralization of the newly formed active parts. 4. Formation of complex molecules of the resulting salt. 5. Possible solidification of the salt.

He concluded that the sum of the generation of heat in processes Nr. 1 and 3 must be constant at the formation of one equivalent of salt. This is the reason why the heat of neutralization of strong acids with strong bases is about constant, and agrees with the experimental values shown in Table 2. Process Nr. 2, the new formation of active from inactive parts, in contrast, is accompanied by the absorption of heat. He expressed it in *Theses* 52, 53, and 56:

*Thesis 52. La transformation de l'état inactif en l'état actif d'un hydrate (faible) est accompagnée par une absorption de chaleur. (52. The transformation from the inactive to the active state of a (weak) hydrate is accompanied by heat absorption.)*

*Thesis 53. A la neutralisation, un acid faible dégage en général moins de chaleur qu'un acide fort. Une proposition analogue est valable pour les bases (On neutralization, a weak acid generally releases less heat than a strong acid. An analogous proposition is valid for bases).*

*Thesis 56. La chaleur de neutralisation déagée par la transformation d'une base et d'un acide parfaitement actifs en eau et en sel non-compliqué, n'est que la chaleur d'activité de l'eau. (The heat of neutralization released at the conversion of a perfectly active base and acid into water and a simple salt is nothing but the heat of activation of the water.)*

The heat of neutralization is therefore a measure for the strength of an acid or a base. For strong acids and bases it is given by the reaction of their active parts, the  $H^+$  and the  $OH^-$  ions of the completely dissociated electrolytes, under formation of the inactive water molecule. This amount corresponds to the heat of activation of water, which is necessary to completely split water into  $H^+$  and  $OH^-$ . This amount is about  $13700 \text{ cal mol}^{-1}$  at  $18^\circ\text{C}$ ,<sup>16</sup> and corresponds to the experimentally found neutralization heat of a strong acid with a strong base. When a weak acid is neutralized with a strong base such as  $\text{NaOH}$ , the inactive part of the acid must be converted to the active, which requires heat absorption. The total heat balance of the reaction is thus less than  $13700 \text{ cal}$ , and its magnitude is the measure Arrhenius had assumed for the strengths of acids. Since the heats

of neutralization correlate with the molecular conductivities, Arrhenius succeeded in confirming his original hypothesis, that is, the results of thermochemistry were the first proof which he had mentioned as a necessity in his Nobel lecture.

He concluded his dissertation with the summary of Part 2, of which we reproduce the key passage. It read

*Dans la partie présente de cet ouvrage, nous avons d'abord fait voir la vraisemblance-de ce que les électrolytes peuvent se rencontrer sous deux formes différentes, l'une active, l'autre inactive, de sorte que la partie active est toujours, dans les memes circonstances extérieures (température et dilution), une certaine fraction de ln quantité totale de l'électrolyte. La partie active conduit l'électricité et est ainsi en réalité électrolytique, mais non pas la partie inactive.*

In the present part of this work, we have first shown the verisimilitude that electrolytes can occur in two different forms, one active, the other inactive, so that the active part is always, under the same external circumstances (temperature and dilution), a certain fraction of the total quantity of the electrolyte. The active part conducts electricity and is therefore actually electrolytic, but the inactive part is not. [Boldface by the author].

This was the first step towards what later became known as the dissociation theory of electrolytes in solutions. He completed his dissertation and submitted it to the Swedish Academy of Sciences.

#### PRESENTATION OF DISSERTATION, ITS LOW GRADING, AND THE CONSEQUENCES

Arrhenius presented his hypotheses in a lecture held at the Royal Swedish Academy of Science on June 6, 1883, and submitted them at Uppsala University in a slightly modified form as dissertation in 1884.<sup>[6, 7]</sup> However, Robert Thalén, the physics professor, and Per Teodor Cleve, the chemistry professor at the university who evaluated the dissertation were not convinced, and Arrhenius' doctoral thesis was given a poor grade. It was awarded a forth class, its defense a third class. This rating was too low to lecture as a docent, and the Uppsala faculty offered him only an unpaid position, what he refused.

Immediately after the disappointing assessment in 1884, Arrhenius sent copies of his dissertation to several European physical chemists, most of whom did not respond,<sup>17</sup> except Wilhelm Ostwald, professor at the

<sup>16</sup> The heat of neutralization depends on the temperature. Thomsen reported that it decreases by  $43 \text{ cal } ^\circ\text{C}^{-1}$ , see footnote 16.

<sup>17</sup> We would like to comment that although the English physicist Sir Oliver Joseph Lodge (1851 – 1940) mentioned above did not contact Arrhenius directly, he subjected the two parts of Arrhenius' dissertation separately to an extraordinary detailed critical analysis of almost every

Riga Polytechnic.<sup>18</sup> Ostwald described his ambivalent judgment to reply or not in Chapter 11 of his *“Lebenslinien: Eine Selbstbiographie”*<sup>[90]</sup> (Lines of Life: A Self-Biography; also Lifelines: An Autobiography) after reading Arrhenius’s dissertation. He found that “the work contained obvious weaknesses (which were also exaggeratedly emphasized by other critics afterwards); so that I still had to reckon with the possibility that those correct results had only turned out that way by chance”.

Ostwald had already executed experiments about the specific affinities of acids and bases. He conducted them during the time Arrhenius was working on his dissertation, but in contrast to him, using various non-electrochemical methods. His investigations, which led to the second proof of Arrhenius’ hypotheses, were a good fortune for Arrhenius. He said retrospectively in his Nobel lecture *“Development of the theory of electrolytic dissociation”* held on December 11, 1903 (we continue with this lecture which we have cited above up to *“etc.”*)

“. . . . . etc. The Norwegian research scientists Guldberg and Waage had developed a theory according to which the strength of different acids could be measured . . . . . by their capacity of increasing the speed of certain chemical reactions. In conformity with this we can suppose that the speed of a reaction produced by an acid is proportional to the number of active molecules in it. I had only a few experiments by Berthelot to demonstrate this law, but in 1884 Ostwald published a large number of observations which proved that this conclusion was correct.”

These observations of Wilhelm Ostwald, to which Arrhenius referred, will be the subject of the following chapter.

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paragraph, thesis and equation in a report of the British Association for the Advancement of Science.<sup>[88]</sup> The entire analysis contained no less than 27 closely printed pages (Part I, p. 357- 362, Part II, p. 362-384.) Lodge pioneered radiotelegraphy and discovered electromagnetic radiation earlier than Heinrich Hertz. He held patents for radio and the moving coil loudspeaker. He was familiar with electrophoresis as well. In 1886, he invented the moving boundary method,<sup>[89]</sup> an electrophoretic method that replaced Hittorf’s method for determining transference numbers. We have described the latter method in detail in Part 3 of our historical review.<sup>[5]</sup> The moving boundary method had the great advantage that the transference numbers could be measured in much less time, with much less effort and without chemical analysis of the constituents in the electrode compartments, at lower cost and, above all, with much higher accuracy. In 1881 he became professor of physics and mathematics at University College Liverpool. From 1900, Lodge was the first rector of the new University of Birmingham. In the late 1880s Lodge developed a keen interest in spiritualism and telepathy and became a member of the Ghost Club. Founded in London in 1862, the Ghost Club is a paranormal research organization. The club is concerned with ghosts and hauntings, but has also studied UFOs, dowsing and cryptozoology.

<sup>18</sup> In the following we will tell more about Ostwald, since he played an eminently important role in Arrhenius’ life.

## 2ND PROOF. OSTWALD’S “STUDIEN ZUR CHEMISCHEN DYNAMIK” (STUDIES ON CHEMICAL DYNAMICS): MOLECULAR CONDUCTIVITY AND AFFINITY COEFFICIENT

Wilhelm Ostwald, born in 1853 in Riga, now capital of Latvia, studied from 1872 chemistry at the University of Dorpat, now Tartu, Estonia. In 1882, at the age of 29, he became a professor at the Riga Polytechnic, where he continued the work he had made in Dorpat.<sup>[91-95]</sup>

From 1882 to 1884 Ostwald, already professor in Riga, published the first three parts of the series on *“Studien zur chemischen Dynamik”* (Studies on Chemical Dynamics) but without knowing about Arrhenius’ dissertation. A photograph of Ostwald taken at the time when he began with these studies is shown in Figure 5.

The goal of Ostwald’s “Studies in Chemical Dynamics” was to determine the relative strengths of acids based on the intensity of an acid’s effect on a base. His aim was to express this intensity by a number which he quoted as “Affinitätsgröße” (affinity value, affinity, in some papers affinity coefficient) of the acid. He determined this affinity from the reaction rate of the acid with the corresponding reactant. In other words, the greater the affinity of an acid in a reaction under unchanged conditions, e.g., at constant temperature and concentrations, the stronger the acid. He chose acids for his new research because he had already done earlier work with these compounds in Dorpat between 1877 and 1881 on other questions and with other methods.<sup>[93-97]</sup>

In his first paper of this series,<sup>[98]</sup> dated December 1882, Ostwald determined the rate of complete conversion of acetamide by different acids, all under the same conditions. For *“Zweite Abhandlung”*<sup>[99]</sup> Ostwald hydrolyzed methyl acetate to acetic acid and methyl alcohol. This reaction was analogous to that described by M. Berthelot and L. Péan de St. Gilles in 1862 for the formation of esters from acids and alcohols.<sup>[100-103]</sup> The subject of *“Dritte Abhandlung: Die Inversion des Rohrzuckers”* (Third Treatise: The Inversion of Cane Sugar)<sup>[104]</sup> was the influence of acids on the rotation of polarized light of cane sugar. Investigations on the course of inversion as a function of reaction time had already been successfully carried out in 1850 by Ludwig Wilhelmy<sup>19</sup> but remained

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<sup>19</sup> Ludwig Ferdinand Wilhelmy (1812 – 1864) was a German physicist and physical chemist. He is considered the first to publish quantitative studies on chemical kinetics. In 1850, using a polarimeter, he measured the conversion of sucrose into fructose and galactose after the addition of acid (we have quoted it in the main text; it is the reaction Ostwald studied in his *Third Treatise*). He formulated the kinetics of the reaction in complex differential equations and published in 1851 the book *“Versuch einer mathematisch-physikalischen Wärme-Theorie”*<sup>[105]</sup> (Attempt of a mathematical-physical theory of heat).



**Figure 5.** Photo of Wilhelm Ostwald from 1882, the year he became a professor at the Riga Polytechnic. Unknown author. Reprinted with permission. © Copyright Gerda and Klaus Tschira Foundation, 2022.

largely unnoticed.<sup>[106, 107]</sup> In 1862 J. Löwenthal and E. Lenssen<sup>[108, 109]</sup> also described the influence of acids on the inversion of sugars.

Ostwald added the corresponding acid solution to a solution of cane sugar and determined the inversion rate from the optical rotation measured with the aid of a thermostated polarization tube. The rate constants were calculated by Wilhelmy's formula.<sup>[106, 107]</sup> This method was the most accurate and the least labor-intensive and time-consuming of the methods used, since it did not require chemical analysis to keep track of its progress. The affinities of the acids obtained by this third treatise agreed sufficiently well with those from the hydrolysis of methyl acetate. This result definitively confirmed the conclusion drawn from the previous treatises that the order of the affinity corresponds to the order of the strengths of the acids. Ostwald thus succeeded in compiling such a list by three independent methods.

Ostwald had just completed the third treatise – it was dated April 1884 – when he received in June 1884 the dissertation Arrhenius has sent to him. He reported in Chapter 11 of his autobiography<sup>[90]</sup> that at this day he had a tooth ulcer, his wife gave birth to their daughter, and, last but not least, he received the dissertation. The tooth ulcer healed, mother and daughter were well, but the dissertation gave him a headache and a restless night. At first he thought the work was nonsense. After closer study, however, he realized that the author had treated and partly solved the great problem of the proportionality of the affinity coefficients of acids and bases

and their electric conductivity in a much more comprehensive way than he had.

We quote a passage from his autobiography which we regard as typical of the integrity of Ostwald's character. He describes with admirable sincerity the moral dilemma he faced. Should he, who was himself working on a new branch of research, prevent a possible competitor, or should he include him? We reproduce in the footnote<sup>20</sup> what Ostwald reported on this.

Immediately thereafter, Ostwald began to measure the molecular conductivities of the acids whose affinity coefficients he had determined in his “Studien zur chemischen Dynamik” described above, and meanwhile informed Arrhenius by letter about his plan. To measure the conductivities, he aimed to apply alternating current according to Kohlrausch's method,<sup>[25]</sup> but did not yet have any equipment available in Riga. He therefore borrowed a resistor box from the Riga telegraph office for a short time, copied it himself in the Polytechnic's workshop, and performed the measurements on his extensive collection of acids, which he possessed from earlier investigations. The measurements were completed in a few days, and he immediately submitted the results for publication to *Journal für praktische Chemie* as “Notiz über das elektrische Leitungsvermögen der Säuren” (Note on the Electrical Conductivity of Acids), dated July 1884.<sup>[110]</sup>

In this publication he held that the rate of chemical reactions depends on the velocity and thus on the conductivity of the ions which are involved. He mentioned that in his “*Studies in Chemical Dynamics*” of 1883

<sup>20</sup> Ostwald wrote: “One can easily imagine what a confusion of feelings such a realization must arouse in a young researcher [Ostwald] who has only to make his future and suddenly finds himself confronted with a highly energetic co-worker in the field which he had chosen so lonely and remote. In addition, the work contained obvious weaknesses ....., so that I still had to reckon with the possibility that those correct results had only turned out this way by chance. For a few days, as in Bürger's ballad, the black and the white companion [Gottfried August Bürger (1747 – 1794) was a popular German poet; author's note] fought over my soul. It was certainly not difficult to keep this sudden competitor in the background by silence, since at present only a few professional colleagues cared at all about such questions. Then, because of the existing errors, one could condemn the whole thing and, besides, the publication in the writings of the Swedish Academy of Sciences was an obstacle for the dissemination anyway, since these hardly came into the hands of the chemists.

So all I had to do was ignore the writing to keep the competitor at bay, if not for good, then for the foreseeable future. ... I did not learn the details of the technique of fighting unwelcome coworkers as well as competitors until later. ... On the other hand, the scientific idealism that I had acquired as a self-evident prerequisite for all work in this highest field of human progress ... was active. ... In addition, the joyful feeling asserted itself to be able to plow a virgin soil shoulder to shoulder with a new fellow worker [Arrhenius], ..., especially since I found him equipped with intellectual working means which I had not used before and which, in combination with those familiar to me, ensured an all the more effective progress. ... “

and 1884 he showed that the rates of reactions affected by acids are proportional to the affinity of the acids as determined by him.<sup>[98, 99, 104]</sup> Therefore, there is also a proportionality between the reaction rates and the electrical conductivity. He pointed out that Svante Arrhenius arrived at the same result by a different route, by that which he published in his dissertation in 1884.

In contrast to the many controversies about the priority of theories by other researchers, Ostwald emphasized with remarkable righteousness on p. 93

*”Dem Autor dieser Abhandlungen, die zu dem Bedeutendsten gehört, was auf dem Gebiet der Verwandtschaftslehre publicirt worden ist, kommt nicht nur die Priorität der Publikation, sondern auch die der Idee zu“* (To the author of these treatises, which belong to the most important what has been published in the field of affinity theory, comes not only the priority of the publication, but also that of the idea.)

Since Arrhenius' dissertation was submitted to the Swedish Academy on June 6, 1883, and published in May 1884, he received it directly from him not until June 1884. He emphasized this chronological order by noting: “I give these details in order, in stating the independence of my efforts in this field from Arrhenius' work, not to fall into the appearance of an unmotivated priority recclamation.”

Ostwald then gave in a table (Table 3) the comparative values obtained by three independent methods. Column I of this table lists the conductivities of the acids measured by him, column II the rate constants of the catalysis of methyl acetate and column III the rate constants for the inversion of cane sugar.

Comparing these values Ostwald concluded

*Eine Übereinstimmung, wie sie die drei Reihen bieten, habe ich selbst nicht erwartet; diesselbe ist wohl geeignet, jeden Zweifel an der Bedeutung der Affinitätsgrößen zu heben. Bedenkt man, dass weder die Temperatur, noch die Verdünnung bei den drei verglichenen Versuchsreihen diesselbe war, so darf man die Uebereinstimmung der drei Reihen, deren Unterschiede im Uebrigen ganz gesetzmässig verlaufen wohl befriedigend nennen. In Bezug auf die weitgehenden Konsequenzen, welche aus diesem Ergebnis gezogen werden können, muss ich auf die oben citirten Arbeiten von S. Arrhenius verweisen. Riga, Juli 1884.* (I myself did not expect an agreement such as that offered by the three series; this is probably suitable to remove any doubt about the significance of the affinity coefficients. Considering that neither the temperature nor the dilution was the same in the three series of experiments compared, one may quote the agreement of the three series, whose differences are otherwise quite lawful, as satisfactory. With regard to the far-reaching consequences which can

Table 3. Column I. records the conductivities of the acids measured by Ostwald after he received the dissertation Arrhenius has sent to him, column II. the rate constants of the hydrolysis of methyl acetate, column III. the rate constants for the inversion of cane sugar. The values were related to  $HCl=100$ . Taken from ref.<sup>[110]</sup>.

	I.	II.	III.
1. Salzsäure, HCl	100	100	100
2. Bromwasserstoff, HBr	101,0	98	111
3. Salpetersäure, HNO <sub>3</sub>	99,6	92	100
4. Aethylsulfonsäure, C <sub>2</sub> H <sub>5</sub> .SO <sub>3</sub> OH	79,9	98	91
5. Isäthylonsäure, C <sub>2</sub> H <sub>5</sub> .OH.SO <sub>3</sub> OH	77,8	99	92
6. Benzolsulfonsäure, C <sub>6</sub> H <sub>5</sub> .SO <sub>3</sub> OH	74,8	99	104
7. Schwefelsäure, H <sub>2</sub> SO <sub>4</sub>	65,1	78,9	73,2
8. Ameisensäure, HCOOH	1,65	1,31	1,58
9. Essigsäure, CH <sub>3</sub> .COOH	0,434	0,345	0,404
10. Monochloressigsäure, CH <sub>2</sub> Cl.COOH	4,90	4,90	4,84
11. Dichloressigsäure, CHCl <sub>2</sub> .COOH	25,3	28,0	27,1
12. Trichloressigsäure, CCl <sub>3</sub> .COOH	62,8	68,2	75,4
13. Glycolsäure, CH <sub>2</sub> OH.COOH	1,34	—	1,31
14. Methylglycolsäure, CH <sub>3</sub> .OCH <sub>2</sub> .COOH	1,76	—	1,82
15. Aethylglycolsäure, CH <sub>3</sub> .OC <sub>2</sub> H <sub>5</sub> .COOH	1,90	—	1,87
16. Diglycolsäure, O(CH <sub>2</sub> .COOH) <sub>2</sub>	2,58	—	2,67
17. Propionsäure, C <sub>2</sub> H <sub>5</sub> .COOH	0,825	0,804	—
18. Milchsäure, C <sub>2</sub> H <sub>4</sub> OH.COOH	1,04	0,80	1,07
19. β-Oxypropionsäure, C <sub>2</sub> H <sub>4</sub> OH.COOH	0,606	—	0,80
20. Glycerinsäure, C <sub>2</sub> H <sub>4</sub> (OH).COOH	1,57	—	1,72
21. Branntraubensäure, C <sub>2</sub> H <sub>3</sub> O.COOH	5,00	6,70	6,49
22. Buttersäure, C <sub>3</sub> H <sub>7</sub> .COOH	0,816	0,900	—
23. Isobuttersäure, C <sub>3</sub> H <sub>7</sub> .COOH	0,811	0,268	0,835
24. Oxysbuttersäure, C <sub>3</sub> H <sub>6</sub> OH.COOH	1,24	0,82	1,06
25. Oxalsäure, (COOH) <sub>2</sub>	19,7	17,6	18,8
26. Malonsäure, CH <sub>2</sub> (COOH) <sub>2</sub>	3,10	2,87	3,08
27. Bernsteinsäure, C <sub>2</sub> H <sub>3</sub> (COOH) <sub>2</sub>	0,581	0,50	0,55
28. Apfelsäure, C <sub>2</sub> H <sub>3</sub> OH(COOH) <sub>2</sub>	1,34	1,18	1,27
29. Weinsäure, C <sub>2</sub> H <sub>2</sub> (OH) <sub>2</sub> (COOH) <sub>2</sub>	2,28	2,30	—
30. Traubensäure, C <sub>2</sub> H <sub>2</sub> (OH) <sub>2</sub> (COOH) <sub>2</sub>	2,63	2,30	—
31. Brenzweinsäure, C <sub>2</sub> H <sub>2</sub> (COOH) <sub>2</sub>	1,08	—	1,07
32. Citronensäure, C <sub>2</sub> H <sub>3</sub> (OH) <sub>2</sub> (COOH) <sub>2</sub>	1,66	1,68	1,78
33. Phosphorsäure, PO(OH) <sub>3</sub>	7,27	—	6,21
34. Arsensäure, AsO(OH) <sub>3</sub>	5,38	—	4,81

be drawn from this result, I must refer to the above cited work of S. Arrhenius. Riga, July 1884).

Immediately after the publication of this Note, Ostwald traveled via Stockholm to Uppsala where he met Arrhenius, and spent three days with lively discussions, and borne of great personal sympathy. They agreed that Arrhenius should come to Riga as soon as possible for joint work. For this, however, Arrhenius first needed his habilitation. Through Ostwald's offer of a position in Riga, Arrhenius was appointed docent in Uppsala. Moreover, Arrhenius received in 1886, with Edlund's support, a three-year traveling scholarship from the Royal Swedish Academy of Sciences to meet leading physicists in Europe.

He first used it for cooperation with Ostwald in Riga in 1886, visited Friedrich Kohlrausch in Würzburg in 1886 and 1887, Ludwig Boltzmann in Graz in 1887 (see the photo in Figure 6), van 't Hoff in Amsterdam in 1888,<sup>21</sup> and again in 1888 Ostwald in Leipzig, where Ostwald became professor of physical chemistry in 1887.

<sup>21</sup> Where he published by support of van 't Hoff "Theorie der isohydri-schen Lösungen"<sup>[112]</sup> concluded March 1888.



**Figure 6.** Photograph taken during Arrhenius' visit of Ludwig Boltzmann in Graz in 1887.<sup>[111]</sup> Date: October 1887. Source Universität Graz. Author unknown. Arrhenius is the fourth from the right, standing behind Boltzmann. Public domain. The photograph shows, standing from the left: Walther Nernst, Heinrich Streintz, Svante Arrhenius, Richard Hiecke. Sitting, from the left: Eduard Aulinger, Albert von Ettingshausen, Ludwig Boltzmann, Ignaz Klemenčič, Victor Hausmanning.

### 3RD PROOF. VAN 'T HOFF'S THEORY OF OSMOSIS

It was a beneficial coincidence that in the midst 1880s Jacobus Henricus van 't Hoff<sup>22</sup> investigated the osmotic pressure between the dilute solution of a solute and the pure solvent, which were separated by a semipermeable membrane. He was referred by the Dutch botanist Hugo de Vries to the work of Wilhelm Pfeffer (1845–1920), then professor of botany in Basle. In 1877 Pfeffer had measured the osmotic pressure,  $P$ , with membranes<sup>23</sup> that were permeable only to water, but not to solutes.<sup>[115]</sup> He found that, at a given concentration,  $P$  is proportional to the absolute temperature,  $T$ ; at a given temperature,  $P$  is inversely proportional to the volume,  $V$ , or proportional to the concentration. Pfeffer describes this dependence by

<sup>22</sup> The Dutch physical chemist Jacobus Henricus van 't Hoff (1852 – 1911) was one of the most renowned scientists of his time. He made important contributions in various fields of chemistry. In addition to the subject treated here, namely the theory of the osmotic pressure of dilute solutions, he proposed the tetrahedral structure of the bonds of the carbon atom, explained optical activity, and developed stereochemistry. He contributed significantly to chemical kinetics and thermodynamic issues. He was the first Nobel Laureate in Chemistry in 1901 “for his discovery of the laws of chemical dynamics and osmotic pressure in solutions.”

<sup>23</sup> Pfeffer produced membranes by placing two different solutions into contact in a cell made of clay. One solution contained copper acetate, the other potassium ferrocyanide. The detailed properties of numerous membranes and the conditions for their formation were described by Moritz Traube in 1867.<sup>[113]</sup> Those used by van 't Hoff are found as experiment No. 145 on page 244 in ref. <sup>[114]</sup>.

$P=kt/V$  or  $PV=kT$ , where  $k$  was a constant of proportionality.

Applying the laws of Boyle, Henry, Gay-Lussac and Avogadro, van 't Hoff deduced that the constant  $k$  is equal to the gas constant  $R$ . The equation for the osmotic pressure read thus  $PV=RT$ . It is expressing the analogy between the osmotic pressure of a compound in solution and the pressure of the compound when it is in the gaseous state under the same conditions, i.e., at the same temperature and in the same volume.

van 't Hoff presented his theory at l'Académie Royal des Sciences de Suède on October 14, 1885 as memoir entitled “*Lois de l'équilibre chimique dans l'état dilué, gazeux ou dissous*” and published it in *Kongliga Svenska Vetenskaps-Akademiens Handlingar*.<sup>[116]</sup> On p. 43 he emphasized this analogy by stating

*La pression exercée par les gaz à une température déterminée si un même nombre de molécules en occupe un volume donné, est égale à la pression osmotique qu'exerce dans les mêmes circonstances la grande majorité des corps, dissous dans les liquides quelconques.* (The pressure exerted by the gases at a given temperature determined if the same number of molecules occupy a given volume, is equal to the osmotic pressure exerted by the great majority of bodies, dissolved in any liquids under in the same circumstances).<sup>24</sup>

Transformed to modern terminology: the osmotic pressure,  $\Pi$ , is directly proportional to the concentration,  $c$ , of the solute, or to the number of dissolved particles per unit volume, respectively. This relation is formally equal to the equation of state of an ideal gas, and reads  $\Pi V=nRT$  ( $n$  is the number of moles) or  $\Pi=cRT$ .<sup>[118]</sup>

However, van 't Hoff found in experiment that the relationship held good for non-electrolytes as solutes, e.g., for glucose, but for electrolytes the osmotic pressures were higher. For such solutions the equation had to be modified to  $PV=iRT$  (now  $\Pi=iRT$ , with  $i$  being the van 't Hoff factor.

For strong electrolytes these factors,  $i$ , were integer numbers, and were equal to the number of ions upon complete dissociation. For electrolytes, e.g., with formula  $AB$ , the van 't Hoff factor was 2, it was 3 for  $A_2B$ , etc. Remarkably, non-integer numbers were measured for weak electrolytes, indicating partial dissociation of molecules into ions and uncharged fractions. It was shown that van 't Hoff factor  $i$  and Arrhenius's degree of dis-

<sup>24</sup> van 't Hoff published in 1866 the very similar, but not the same paper “*L'équilibre chimique dans les Systèmes gazeux ou dissous à l'état dilué*” in Archives Néerlandaises.<sup>[117]</sup>

sociation  $\alpha$  are related to each other.<sup>25</sup> For Arrhenius, the results of van 't Hoff's osmotic pressure theory were the most convincing confirmation of the theses of his dissertation.<sup>26</sup> This was the third proof and the decisive step towards a well-founded dissociation theory.

Ostwald was highly dissatisfied with the fact that the journals established in the 1880s published scientific papers in the field of physical chemistry mostly intermingled with publications covering a wide variety of fields. In his opinion, papers on physical chemistry topics did not receive the attention they deserved. He therefore decided to found a new journal focusing on the field of physical chemistry, and published the first issue of this "*Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre*,"<sup>27</sup> in 1887 with van 't Hoff as co-editor and with the collaboration of the most prestigious European scientists. It was, like the following issues, a resounding success.

This journal offered Arrhenius a platform for the distribution of his theory, including explanatory state-

ments for the unconvinced readers. Ostwald published Arrhenius' paper on electrolyte dissociation<sup>[8]</sup> in this first volume.<sup>28</sup>

THE THEORY: "UEBER DIE DISSOCIATION DER IN WASSER GELÖSTEN STOFFE" (ON THE DISSOCIATION OF COMPOUNDS DISSOLVED IN WATER)

Arrhenius' seminal publication on the dissociation of dilute electrolytes<sup>[8]</sup> essentially contained the results of his dissertation and the proofs we have already discussed above. So we will only briefly repeat these parts.

It is noticeable that he did not present the theory chronologically, that is, not with the theses of his dissertation that electrolyte molecules are divided into an electrically active and an inactive part even when no current passes the solution. The reason for this may have been that many chemists were skeptical of Clausius' hypothesis of free ions, which Arrhenius considered one of the precursors of his theory. Arrhenius began his publication with van 't Hoff's theory of the osmotic pressure exerted by dilute solutions of any substance on semi-permeable membranes<sup>[116, 117]</sup> which is described above in the 3rd proof. Its decisive result was that a factor, the van 't Hoff factor  $i$ , has to be introduced. It was an integer or a fractional number, and depended on the number of all dissolved particles in the solution which, as it was believed also by Ludwig Boltzmann,<sup>[121]</sup> "bombard" the membrane.

Arrhenius went on to consider the activity coefficient as defined after *Thesis 15* in his dissertation, symbolized by  $\alpha$  and called degree of dissociation in his dissociation theory.  $\alpha$  can be determined from the ratio of the molecular conductivity  $\Lambda_d$  of the diluted solution and the limiting molecular conductivity,  $\Lambda_o$  as  $\alpha = \Lambda_d / \Lambda_o$ . He showed, as also proved by Kohlrausch, that at the limit of infinite dilution there is complete dissociation. In this case  $\alpha = 1$ , at lower dilution  $\alpha < 1$ . Arrhenius

<sup>25</sup> van 't Hoff wrote about these deviations of the osmotic pressure for solutions of electrolytes from Avogadro's law, that Arrhenius pointed out by letter to him the connection of factor  $i$  with the degree of dissociation (ref. <sup>[118]</sup>, p. 501.)

<sup>26</sup> van 't Hoff's theory of the osmotic pressure offered the theoretical explanation of the observations of the lowering of the freezing point of solutions with different solutes by François-Marie Raoult in 1882. <sup>[15]</sup> Raoult measured this lowering with six different solvents and about two hundred compounds as solutes and found empirically (transl. from French)

<sup>(i)</sup> All bodies, on dissolving in a definite liquid compound which can solidify, lower the freezing point. (ii) In all liquids, the molecular lowering of the freezing point due to the different compounds approaches two values, invariable for each liquid, of which one is double the other. (iii) The normal molecular lowering of the freezing point varies with the nature of the solvent. (iv) One molecule of any compound dissolved in 100 molecules of any liquid of a different nature lowers the freezing point of this liquid by a nearly constant quantity, close to 0.62 degrees. If water is the solvent, and molar concentrations are taken, Raoult's law can be expressed as: When one mole of particles is dissolved in one kilogram of water, its freezing point decreases by 1.86°C (if dissolved in 100 g water, the freezing point decreases by 18.6°C). The corresponding temperature difference is called the molar freezing point depression. This effect is independent of the type of the solute. It holds good only for very dilute solutions. Note that Arrhenius will make use of it in his dissociation theory which he publishes in 1887. We clarify the depression by an example, because the relation between concentration and temperature is sometimes given confusingly. Strong electrolytes consisting of two univalent ions give the molecular depression  $2 \times 1.85 = 3.7$ , those consisting of one bivalent ion with two univalent ions give  $3 \times 1.85 = 5.55$ , those of one tetravalent ion with three univalent ions give  $4 \times 1.85 = 7.4$ , etc. Non-electrolytes give 1.85°C depression (the difference between 1.85 and 1.86 is insignificant in practice).

<sup>27</sup> In 1928 the title was shortened to *Zeitschrift für physikalische Chemie* and a new numbering was assigned, in 1954 the numbering was changed again, since 1979 the journal is published with the subtitle *International journal of research in physical chemistry and chemical physics*.

<sup>28</sup> Remarkably, Max Planck published in the same volume a theory of dissociation independent of Arrhenius and based on thermodynamics, entitled "Über die molekulare Beschaffenheit verdünnter Lösungen" (On the molecular nature of dilute solutions), in which he dealt mainly with Raoult's law of freezing point depression.<sup>[119]</sup> He introduced a constant  $i$ , the *decomposition coefficient*, of dissolved molecules, which was identical with van 't Hoff's constant  $i$  calculated for aqueous solutions of various substances, but had a different physical meaning there. Unlike Arrhenius, Planck did not link his theory to electrical conductivity. It was therefore less general and received little attention. To remain in the context of what are now called colligative properties, it should be mentioned that Planck, in the paper "Über den osmotischen Druck"<sup>[120]</sup> from 1890, showed that both the existence and the magnitude of osmotic pressure follow directly from the same general thermodynamic principles that underlie the laws of vapor pressure and freezing point of a solution, without reference to molecular conceptions.

showed that if  $\alpha$  is known, the factor  $i$  could be deduced as follows.

If  $m$  is the number of inactive molecules,  $n$  the number of active molecules, and  $k$  the number of ions into which each active molecule splits, then  $i=(m+kn)/(m+n)$ . Consequently, since  $\alpha=n/(m+n)$ , the relation between  $i$  and  $\alpha$  reads  $i=1+ \alpha(k-1)$ , and can be calculated from the known value for  $k$  and the measure value for  $\alpha$ . Second, the van 't Hoff factor  $i$  can be determined from Raoult's law of freezing point depression, i.e., from the freezing temperature  $t$ , as  $i=t/18.5$ . Arrhenius thus had two independent methods to obtain the van 't Hoff factor and to compare their agreement. The values for 24 compounds out of a total of 86 which were calculated by the above methods are shown in Table 4.

By comparing the values of  $i$  for the individual compounds in the 4th and the 5th columns of the table, Arrhenius observed indeed a pronounced agreement of most of them (the deviations of copper and cadmium salts were explained by their tendency to form complex molecules). He thus concluded that the following hypotheses to calculate the figures were correct. (1) van 't Hoff's law is valid not only for the majority, but for all compounds, that is to say, also for electrolytes in aqueous solutions. (2) Each electrolyte in aqueous solutions consists partly of active molecules and partly of inactive molecules. The inactive molecules are converted into active ones when diluted, with the effect that only active molecules are present in solutions under the limiting condition of infinite dilution. This led to the 3rd proof of his hypothesis.

After a discussion of possible objections of chemists, which essentially concerned the effect of molecular complexes, Arrhenius gave further evidence of the validity of his theory, which he summarized under the concept of additivity of physical properties, and which we have not explicitly discussed as 4th proof in the previous part of this text.

Arrhenius considered the properties of dilute salt solutions as additive when the sum of the properties of the parts of the solution, that is the solvent and the parts of the molecules which actually coincide with the ions, is equal to the property of the solution. These additive properties are physical in nature and can be expressed in numerals. Arrhenius cited the following additive properties in favor of his theory.

1. The conductivity. Its additive property was described in 1879 by Kohlrausch in his law of independent ion migration.<sup>[23]</sup> The conductivity of a salt solution is therefore the sum of the conductivities of the positive and negative ions. That of water as a solvent is usually negligible, except in extremely dilute solutions (see ref.<sup>[122]</sup> and the discussion about pure water in Part 3 of our

**Table 4.** Comparison of the van 't Hoff factors,  $i$ , for dilute aqueous solutions of non-conductors, bases, acids and salts, derived from Raoult's freezing point depression,  $t$  (column 4) and from its relation to the degree of dissociation,  $\alpha$ , as given in the above text (column 5).  $\alpha$  was measured from the ratio of the conductivities of the dilute solution and those at limiting conditions. Temperature  $t$  is in °C. The paper lists a total of 90 solutes.

SUBSTANCE	FORMULA	$\alpha$	$i=$ $t/18.5$	$i=$ $1+(k-1)\alpha$
<b>NON-CONDUCTORS</b>				
Methyl alcohol	$CH_3OH$	0.00	0.94	1.00
Phenol	$C_6H_5OH$	0.00	0.84	1.00
Acetone	$C_3H_6O$	0.00	0.92	1.00
Acetamide	$C_2H_3ONH_2$	0.00	0.96	1.00
<b>BASES</b>				
Lithium hydroxide	$LiOH$	0.83	2.02	1.83
Sodium hydroxide	$NaOH$	0.88	1.96	1.88
Ammonia	$NH_3$	0.01	1.03	1.01
Methylamine	$CH_3NH_2$	0.03	1.00	1.03
<b>ACIDS</b>				
Hydrochloric acid	$HCl$	0.90	1.98	1.90
Nitric acid	$HNO_3$	0.92	1.94	1.92
Sulphuric acid	$H_2SO_4$	0.60	2.06	2.19
Hydrogen sulphide	$H_2S$	0.00	1.04	1.00
Boric acid	$B(OH)_3$	0.00	1.11	1.00
Hydrocyanic acid	$HCN$	0.00	1.05	1.00
Formic acid	$HCOOH$	0.03	1.04	1.03
Acetic acid	$CH_3COOH$	0.01	1.03	1.01
<b>SALTS</b>				
Potassium chloride	$KCl$	0.86	1.82	1.86
Ammonium chloride	$NH_4Cl$	0.84	1.88	1.84
Potassium cyanide	$KCN$	0.88	1.82	1.82
Sodium acetate	$CH_3COONa$	0.79	1.73	1.79
Ammonium sulphate	$(NH_4)_2SO_4$	0.59	2.00	2.17
Copper sulphate	$CuSO_4$	0.35	0.97	1.35
Mercuric chloride	$HgCl_2$	0.03	1.11	1.05
Cadmium iodide	$CdI_2$	0.28	0.94	1.56
Cadmium nitrate	$Cd(NO_3)_2$	0.73	2.32	2.46

series<sup>[5]</sup>). However, this applies only to so-called strong electrolytes, that is, completely dissociated compounds such as the salts of monobasic acids and the strong acids and bases. For weak acids and bases, e.g. for acetic acid, hydrocyanic acid and ammonia, the additivity does not apply, except for extremely dilute solutions for the reasons already mentioned above.

2. The heat of neutralization in dilute solutions. This has already been discussed in the chapter about the 1st proof above.

3. The specific volume and the specific gravity of dilute salt solutions. Claude-Alphonse Valson reported

1871 that the specific gravity (which is the ratio of the density of an object, and a reference substance), is an additive property.<sup>[123]</sup>

4. The specific refractive power of solutions. It was shown by John Hall Gladstone in 1863 that the so-called refractive equivalent is an additive property.<sup>[124]</sup> This additivity also applies to dilute aqueous solutions of dissociated electrolytes.

5. The capillarity phenomena. They are, according to Valson<sup>[125]</sup> additive properties of solutions of salts. However, since they can be traced back to the specific gravity they required no further justification.

6. The freezing point depression. Its additivity by salts in water was discussed in 1885 by Raoult.<sup>[126]</sup> Some properties are proportional to the freezing point depression. Guldberg<sup>[127]</sup> and van 't Hoff<sup>[116]</sup> showed this for the lowering of the vapor pressure, and the osmotic pressure, Hugo de Vries for the isotonic coefficient.<sup>[128]</sup>

With this additional evidence for his theory, Arrhenius completed his seminal paper.

Ostwald promoted Arrhenius' dissociation theory, nonetheless many chemists initially disapproved it. Their objections were mainly the same which were already directed against Clausius' theory, and which Arrhenius had tried to present as untenable in his dissertation in Part 2 on pages 6 and 31. In passing, it should be mentioned that Ostwald first actively defended the theory in 1888 in his articles in volume 2 of the same journal,<sup>[129]</sup> <sup>[130]</sup> in 1889 with W. Nernst in the joint paper "Über freie Ionen" (On free Ions) in volume 3,<sup>[131]</sup> and in many other papers and at various occasions. We have described in Part 3, p. 97-98, of the present series<sup>[5]</sup> that in this 1889 paper capillary electrophoresis was performed in one of four occasions in the entire 19th Century.

Beside his pioneering theory, Arrhenius contributed with numerous publication on this subject. In the years from 1887 to 1889, he published eight papers.<sup>[112, 132-139]</sup> in addition to the following attacking "Electrolytic Dissociation versus Hydration"<sup>[140]</sup> from 1889. It was addressed to the proponents of the prevailing hydrate theory, English chemists who vehemently rejected his theory.<sup>29</sup> This "early" hydrate theory dates back to the 1810s and is probably not known in detail to today's chemists. It is not to be confused with the modern hydrate theory, which is now known to every chemist and physical chemist.

The followers of the early hydrate theory, most notably Henry Edward Armstrong and Spencer Umfreville

Pickering, considered Arrhenius' assumption that anhydrous ions exist in aqueous solutions to be incompatible with their theory.<sup>30</sup> They suspected that, especially in highly dilute solutions with their extreme excess of water, the dissociation theory was in conflict with the law of mass action.

In 1903, about fifteen years after the publication of his theory, Arrhenius received the Nobel Prize in Chemistry "in recognition of the extraordinary services he has rendered to the advancement of chemistry by his electrolytic theory of dissociation."<sup>31</sup> It is therefore somewhat surprising that some advocates of the hydrate theory held to their strict rejection of electrolyte dissociation decades after the Nobel Prize was awarded. We will not finish thus the story about this rejection without mentioning that, as reported in ref. <sup>[141]</sup>, p. 1559, even in the 1930s Prof. Louis Albrecht Kahlenberg<sup>32</sup> taught electrochemistry at the University of Wisconsin disregarding the existence of ions in solutions.

Early hydrate theory and transformation of its parts into the modern one arguably deserved its own historical overview because of the decades-long importance of the former and its role in combating dissociation theory, especially since it has fallen into oblivion.

## SUMMARY

When in the early 1880s the Swedish doctoral student Svante Arrhenius decided to investigate the electrical conductivity of highly diluted electrolyte solutions as the subject of his dissertation there were hardly any studies on this topic in the literature. Most of them were published by his 18 years older contemporary Friedrich Kohlrausch, who had been measured conductivities at

<sup>30</sup> Indeed Arrhenius stated verbatim on p. 32 of his 1889 pamphlet [author's note:  $n$  is the number of water molecules that form complexes of defined stoichiometry with a salt molecule]: "But as we have no ground for attributing any particular value to  $n$ , and as it is besides probable that many salts (e. g. most of those of potassium) exist only in the anhydrous state, the simplest and likeliest assumption is that the ions of the salts, and consequently the salts themselves, exist in solution without water of hydration."

<sup>31</sup> To Wilhelm Ostwald the Nobel Prize in Chemistry 1909 was awarded "in recognition of his work on catalysis and for his investigations into the fundamental principles governing chemical equilibria and rates of reaction."

<sup>32</sup> Louis Albrecht Kahlenberg (1870 – 1941), a US American chemist, was professor of physical chemistry at the University of Wisconsin, where he taught and carried on research for forty-seven years until his retirement in 1940. Beside others, his scientific area was ion conductivity in non-aqueous solutions. Politically, he was opponent of America's entry into World War I, which was unnecessary in his opinion. He was a doctoral student of Wilhelm Ostwald at the University of Leipzig, where he received a PhD, but rejected Arrhenius's dissociation theory.

<sup>29</sup> The paper was communicated by himself in English; an exception, since he usually published in German, and preferably in Swedish in Kongl. Svenska Vetenskapsakademiens Handlingar, Bihang till Kongl. Vetenskapsakademiens Handlingar and in Öfversigt öfver Kongl. Vetenskapsakademiens Förhandlingar.

higher concentrations, and extended his measurements to highly dilute solutions in these years.

At first glance, the completely different ways in which Arrhenius and Kohlrausch conducted their experiments and interpreted their results are striking. Kohlrausch was known for his extremely careful execution of his experiments, for the search and elimination of possible sources of error, and the associated time-consuming and labor-intensive investigation of the solutions with the intention of obtaining the most accurate measurement results possible. These exceptionally accurate data allowed him to derive empirical equations from them (see, e.g., ref. <sup>[5]</sup>) Arrhenius carried out his conductivity measurements in a contrary manner. He did not attach any particular importance to the high accuracy of his measurements, but rather intuitively detected a certain tendency from the data obtained, from which he derived hypotheses rather than empirical laws.<sup>33</sup>

As part of his dissertation Arrhenius measured the electrical resistances of dilute solution from about fifty different electrolytes, and calculated their molecular conductivities as a function of their dilution. He summarized his observations and his conclusions in 56 theses, of which we quote some of the most important. He recognized that the strongest acids – he examined only 5 – were those with the highest molecular conductivity. He observed that the molecular conductivity increased with increasing dilution, and he distinguished two different groups of electrolytes. In the first group, the strong electrolytes, the molecular conductivity increased very little and almost linearly with dilution, approaching the maximum value under limiting conditions. It was assumed that this increase was due to decreasing frictional resistance between the electrolyte molecules as their distances increased with dilution. The second group, the weak electrolytes, behaved completely differently. Their molecular conductivity initially remained at a low level with increasing dilution, but increased abruptly at sufficient dilution. Arrhenius could not initially explain this deviant behavior because there was no reason to attribute it to the frictional effects mentioned above.

Kohlrausch remained essentially with the investigation of the strong electrolytes. However, the said deviant behavior aroused the special interest of Arrhenius. To explain this effect, he made the bold hypothesis that the number of conducting molecules had to increase by splitting the electrolyte molecules into two parts. One part is electrically active, it conducts electricity, the second, electrically inactive part is non-conducting. He further hypothesized that with increasing dilution, the proportion of active parts increases at the expense of the inactive ones. At infinite dilution, all inactive parts are completely dissociated, a verb Arrhenius avoided to use in his dissertation. Arrhenius introduced the activity coefficient (later called degree of dissociation), which indicates the proportion of active molecules to the number of all molecules, if these were completely dissociated. The active parts must be capable of double decomposition, since a permanent exchange with those of other molecules takes place, which – in the absence of an electric potential – leads to a circular current of the ions in the solution. Arrhenius' hypothesis explained both, the high molecular conductivity of the strong acids, as they consist of the electrically active molecules, and the behavior of the weak acids with their initially small activity coefficient that increases sharply with increasing dilution.

To confirm his hypothesis, Arrhenius borrowed results from thermochemistry, especially those of the Dutch physicist Julius Thomsen. Thomsen had determined the heats of neutralization of acids in their reaction with a strong base. He found that strong acids evolve the largest heats of neutralization, weak acids develop smaller heats. These results were consistent with the Arrhenius hypothesis, since strong acids, like strong bases, already consist of the active  $H^+$  and  $OH^-$  ions (their counterions do not contribute to the neutralization), which combine directly to form the inactive water and release its activation energy. In the case of weak acids, in contrast, the inactive part must be transferred into the active part for neutralization, a process that absorbs heat and reduces the heat balance accordingly. This was the first proof of the Arrhenius hypothesis, which was based on a non-electrical thermochemical phenomenon.

Arrhenius, however, was of the opinion that the conductivities measured by him and the heats of neutralization were not sufficient for a solid theory. Without conducting any further experiments himself, he found three more proofs to confirm his hypothesis. The next, the second proof resulted from Wilhelm Ostwald's studies of the affinities of different acids on bases. Ostwald's measurements concerned the kinetics of chemical reactions and the influence of the strength of the acids,

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<sup>33</sup> This difference was emphasized by the above mentioned English inventor of the moving boundary method<sup>[89]</sup> whom we also mentioned in Part 3 of our previous historical article. In a critical commentary in ref. <sup>[115]</sup> Lodge began his analysis – not very encouragingly for Arrhenius – with “Whatever may have been the importance of the first part of this memoir at the date of its appearance (1883), the publication last October in Wiedemann's *Annalen* of a masterly memoir by Prof. F. Kohlrausch on the same subject throws it into the shade; for there can be no doubt that while the ground covered by both is similar, the Kohlrausch memoir is greatly superior, both in the experiments made and in the discussion upon them.”)

which determines their reaction rate. Among others, he investigated the effect of about forty different acids on the reaction rates of hydrolysis of methyl acetate, and on the inversion of cane sugar. After reading Arrhenius dissertation which he received in 1884, he concluded that the stronger an acid is, the more pronounced its affinity should be, as indicated by its molecular conductivity. Thus, Ostwald measured the molecular conductivities of diluted solutions of his acids, and found an astonishing high parallelism with the rate constants. This was the second proof of Arrhenius' hypothesis: it was based on chemical kinetics.

Perhaps the most important piece of evidence was the analogy found by J. H. van 't Hoff between the osmotic pressure exerted on a semipermeable membrane by a dilute solution and the pressure of a gas composed of the same number of particles. This pressure depends only on the number of dissolved particles, but is independent of their electric charge. The deviation of the osmotic pressure from that of Avogadro's law is expressed by van 't Hoff factor  $i$ , which is the number of all solute particles. On the one hand,  $i$  can be determined experimentally by Raoult's freezing point depression. On the other hand, it can be calculated with the aid of Arrhenius' degree of dissociation,  $\alpha$ . If the values of  $i$  obtained from both methods agree, the value for  $\alpha$  is correct, and Arrhenius' dissociation hypothesis is confirmed. The actual agreement found was the third proof. In addition, the additivity of physical properties, such as the specific gravities of solutions confirmed the hypothesis.

Based on these four proofs, Arrhenius had successfully developed the seminal theory "Ueber die Dissociation der in Wasser gelösten Stoffe" in 1887 from the collection of the 56 theses of the 1884 dissertation.

Finally, we would like to address an apparent discrepancy between the subject of our article series – the history of the basic principles of capillary electrophoresis – and that of the present Arrhenius dissociation theory. Although the most important properties studied by Arrhenius were the conductivities of electrolyte solutions, neither his dissertation nor his dissociation theory gives any indication of the associated mobility of ions in free solution under the influence of an electric field. Since this ion mobility is a central property in electrophoresis, one could assume at first glance that the dissociation theory has only little significance for electrophoresis. However, the opposite is the case, as it allows to express the conductivity and thus the mobility over the whole range from zero to its maximum value by means of the degree of dissociation, which can take all values between zero and unit. For this reason, the dissociation

of weak electrolytes described by Arrhenius will certainly be of great relevance in the practice of ion electrophoresis. It will be indispensable for electrophoresis as a future separation method. In this respect, its detailed treatment in this article was justified.

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