Chapter 3
Matter and Electricity

> *In a great number of the cosmogonic myths the world is said to have developed from a great water, which was the prime matter. In many cases, as for instance in an Indian myth, this prime matter is indicated as a solution, out of which the solid earth crystallized out.*
>
> *(Svante Arrhenius)*

3.1 The Association of Matter and Electricity

The beginning of the nineteenth century witnessed the appearance of Volta's pile that gave rise to an explosion of research on the decomposition of chemical substances by means of electricity, although the mechanisms of production of the electric current and of electrolysis still remained a mystery. However, the research of Humphry Davy and Jöns Jacob Berzelius and, above all, the quantitative laws of Michael Faraday, establishing the direct proportionality between the quantity of decomposed compound and the amount of electricity used, made clear that the electric charges were directly attached to the atoms.

Faraday, a great specialist in neologisms, in collaboration with William Whewell (1794–1866), scientist, historian, and science philosopher, invented a number of technical terms used in electrochemistry such as *electrolysis, electrolyte, electrode, anode, cathode, ion, anion,* and *cation*. Nevertheless, the passage of current in electrolytic cells was far from understood. The most difficult problem concerned the electrolysis of aqueous solutions – the electrolysis of molten salts did not present great theoretical complications. Davy in fact succeeded in 1807 in preparing sodium and potassium by means of electrolysis using melted soda and potash at high temperature and platinum electrodes, and in 1808 he isolated barium and strontium by electrolysis using mercury electrodes. Strangely enough, by electrolysis of aqueous solutions, for instance, of sodium sulfate, instead of the elements, one always obtained oxygen and hydrogen! Furthermore, it was difficult to accept that two substances like chlorine and sodium, fiercely reactive if put into

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contact, could peacefully coexist in solution in the form of ions, even if one was negatively and the other positively charged.

A somehow acceptable explanation had been put forward by the London chemist and physicist John Frederic Daniell (1790–1845), a great friend of Faraday, who in 1831 became the first professor of chemistry at King's College of London. Daniell was well known because in 1836 had invented an electrical battery more powerful than that of Volta. Convinced, as Davy, that acidity did not depend on the presence of hydrogen and oxygen in the molecule but only on the reciprocal positions of the parts, he suggested that the appearance of hydrogen and oxygen at the electrodes was not due to the current but instead was caused by a secondary reaction at the electrodes.

Adopting the nomenclature of the time, he wrote that sodium sulfate was formed from Na and (S + 4O) ions. The latter reacted with water HO at the anode producing oxygen according to the chemical equation

$$(\mathrm{S}+4\mathrm{O})+\mathrm{HO}=[(\mathrm{S}+4\mathrm{O})+(\mathrm{H})]+\mathrm{O}\uparrow$$

whereas, at the cathode, the reaction taking place was

$$\mathrm{Na}+\mathrm{HO}=(\mathrm{Na}+\mathrm{O})+\mathrm{H}\uparrow .$$

The first formulation of a theory of electrolysis that took into account atomic motion in solution was presented in 1806 by Theodor von Grotthuss (1785–1822), descended from an old family of the Kurland nobility. Grotthuss, who spent a good part of his short life in his mother's estate in Latvia, grew up in the cultural tradition of the Kurland aristocracy but, thanks to the education received later in Paris during the period 1803–1805, he discovered the existence of Volta's pile and became a confirmed admirer of French science.

However, Grotthuss developed the greatest part of his research in Italy at Naples and Rome in the period 1805–1806. He wrote his theory of electrolytes in French during his stay in Rome in 1805 and published it in 1806 (Grotthuss 1806). In this paper, immediately translated into German and English, Grotthuss proposed a theory of current conduction in water that seems astonishing for the historical period in which it was formulated if one takes into account that the concept of ions was not yet clear and that the formula for water was written HO rather than H_2O. Grotthuss considered a solution as made by chains of polarized water molecules

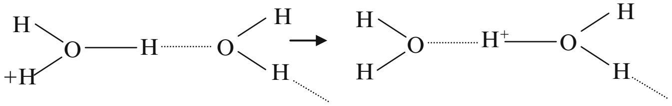
$$\mathrm{O^-H^+}\cdots\mathrm{O^-H^+}\cdots\mathrm{O^-H^+}\cdots\mathrm{O^-H^+}\cdots\mathrm{O^-H^+}\cdots\mathrm{O^-H^+}\cdots\mathrm{O^-H^+}\cdots\mathrm{O^-H^+}\cdots\mathrm{O^-H^+}\cdots\mathrm{O^-H^+}$$

connecting the anode to the cathode. Current flow and the transfer of matter at the electrodes took place due to the instantaneous and cooperative displacement of a hydrogen atom from one molecule to the next. At the anode, the first oxygen ion of the chain was discharged, leaving one oxygen atom free and the hydrogen atom following it in the chain was then bound to the oxygen ion on its right in the chain

$$H^+O^- \cdots H^+O^- \cdots H^+O^- \cdots H^+O^- \cdots H^+O^- \cdots H^+O^- \cdots H^+O^- \cdots H^+O^- \cdots H^+O^- \cdots H^+$$

which, in turn, produced at the right extremity of the chain a free hydrogen ion that was discharged at the cathode, eventually creating a hydrogen atom.

Grotthuss's conduction mechanism offered important hints to the theory of electric conduction in solution. First of all the model of the force field that Faraday modified and transformed in the concept of electric and magnetic fields and of lines of force arises from it. In addition it contributed to the modern formulation of electrical conductivity that correctly explains the great mobility of hydrogen ions in aqueous solutions. The mechanism consists in a series of cooperative jumps of H^+ ions from one molecule of water to the next by means of the formation of H_3O^+ molecules according to the scheme



which is completely different from the classical Brownian motion of the H^+ ion.

A direct consequence of the cooperative jumps of H^+ ions from one water molecule to another in the Grotthuss model was that the ions moved with the same speed in both directions. In 1844, John Daniell, in collaboration with William Allen Miller (1817–1870), new professor at King's College, using a cell divided into three sections – anodic, cathodic, and central – separated by porous walls, found that the solute concentration around the electrodes was different and that the number of cations at the cathode was larger than the number of anions at the anode. The conclusions reached by Daniell and Miller were experimentally confirmed by Johann Wilhelm Hittorf (1824–1914), professor of physics at the University of Münster, who in the years 1853–1859 studied the ionic motion due to an electric current and proved that in electrolysis the current was not transported with the same speed by anions and cations. On the basis of these results, he defined the transport number as the fraction of current transported by each ionic species present in solution (Hittorf 1853), computed the transport number for different types of ions from measurements of the variation of concentration at the electrodes during the electrolysis, and in 1869 formulated his law concerning the migration of ions in solution (Hittorf 1859) These measurements, made at very low current intensity, convinced electrochemists that it was unnecessary to spend energy to ionize the molecules in solution.

The concept of electrolytic dissociation was, however, in the air even if not yet directly formulated. It was, however, anticipated in 1851 in a famous paper of Williamson on the formation of ethers (Williamson 1850). Williamson had suggested that, in an aggregate of molecules of any compound, there was always a continuous exchange of the relative positions of the constituent elements.

For instance, in hydrochloric acid, no hydrogen atom was ever motionless, bound to a given chlorine atom, but was in continuous motion, exchanging position with other hydrogen atoms. In 1857, Clausius, used to thinking in terms of the kinetic theory of gases of molecules in motion, continuously bumping into each other, had no difficulty in accepting this idea and proposing that in solution some ions were already there before the passage of current. The merging of the ideas of Williamson with those of Clausius gained the enthusiastic agreement of Hittorf who saw perfect parallelism between the kinetic theory of gases and solutions, parallelism that also influenced the work of van't Hoff on osmotic pressure (van't Hoff 1887, 1888).

The measurement of conductivity of a solution at first presented two significant difficulties. The first was the high resistivity, a difficulty overcome in the 1830s with the invention of the Wheatstone bridge in 1833 by Samuel Hunter Christie (1784–1865) and improved in 1843 by Sir Charles Wheatstone (1802–1875). With the help of the Wheatstone bridge, it became much simpler to measure the resistivity (inverse of conductivity), even of dilute solution with very low conductivity.

The second difficulty was connected with the fact that, using direct current, the electrolytic cell became polarized due to the accumulation of material at the electrodes with a consequent increase in resistivity. This problem was brilliantly resolved in 1868 by one of the greatest experimental physicists of all times, Friedrich Wilhelm Georg Kohlrausch (1840–1910) by the use of alternating current. Kohlrausch was a central figure in the history of electrochemistry at the end of the nineteenth century. The experimental techniques that he accurately devised and described spread from his laboratories at Göttingen, Zurich, and Darmstadt to the whole of Europe (Kohlrausch 1880). Arrhenius, Ostwald, and van't Hoff, the most important creators of ion theory, developed their research along Kohlrausch's line of experimental measurements.

In 1874, Kohlrausch showed that electrolytes possess a definite and constant value of molecular conductivity λ and by studying conductivity variation with concentration, determined the speed of ionic transfer in solution.

From 1875 to 1879, he examined several solutions of salts and acids and established that each type of ion has its own specific electric resistance, independent of the type of molecule from which it derives (Kohlrausch and Grotrian 1875). He also showed that in the case of slightly dissociated weak electrolytes, molar conductivity increases with dilution due to the increase of dissociation up to a limiting value Λ_0 (Kohlrausch 1885). By studying the conductivity of two electrolytes with a cation or an anion in common, he proved that the limiting conductivity Λ_0 at infinite dilution is the sum of two constant values, $\lambda_0{}^+$ relative to the cation and $\lambda_0{}^-$ to the anion, since in these conditions the behavior of an ion is independent from that of its counterions. In addition, he proved that ions move with their own definite speed, independent of other ions present, defining the law of the independent migration of ions that bears his name (Kohlrausch 1880).

The development of the theory of electrolytic dissociation is, however, tied to the names of two great personalities that played a central role in the development of chemical physics at the end of the nineteenth century: Wilhelm Ostwald and his pupil Svante Arrhenius.

Wilhelm Ostwald (1853–1932), born at Riga, at that time part of the Russian Empire, was educated at Dorpat University (today Tartu) at the extreme limit of the Baltic zone of Europe. During that period, Latvia was a Russian territory, but the dominant culture was German, and teaching was strongly oriented toward the study of physics even in chemistry courses. He therefore avoided the teaching of organic analysis and synthesis that led to the success of the great French and German schools of chemistry of the time. This type of unconventional university training at the periphery of German academic culture was fundamental to his scientific career and responsible for his successes and failures.

As he said later, if he had been born in Germany he would have unavoidably become a boring organic chemist. Ostwald was in fact convinced that his isolation from the principal stream of European research, organic chemistry, had pushed him into getting interested in an unfashionable topic of his time, chemical physics.

After graduation, he obtained the position of assistant at the Physics Institute of Riga directed by Arthur von Oettingen (1836–1920), later moving to the chemistry laboratory of Carl Schmidt (1822–1894), a student of Liebig and Wöhler. Oswald was always very attached to his teachers for the kind of teaching received. Schmidt's assistant, Johann Lemberg (1842–1902), taught him chemistry and introduced him to the concepts of affinity, chemical equilibrium, and reaction rate.

Ostwald selected just the affinity problem for his *Kandidatenschrift* in 1875, based on the study of bismuth chloride solutions. In 1877, he was accepted as a teacher without salary in his own university and in 1881 was hired as ordinary professor of chemistry at the Polytechnic of Riga. In 1887, he became professor of chemical physics at Leipzig where he settled for life, apart for a short interruption in the period 1904–1905 when he was invited to the United States as first "Exchange Professor" at the University of Harvard.

Ostwald was the true founder of modern chemical physics, not only as a researcher but also as a great organizer and research talent scout. His teaching and research activity was impressive. At 50 years, he had already supervised the theses of 147 students, 34 of who later became university professors. His school attracted researchers from all over Europe as well as from the United States. Among his best known pupils there were three Nobel laureates, Van't Hoff, Arrhenius, and Nernst; Wislicenus, one of the fathers of stereochemistry; Gustav Tammann (1861–1922) a Russian also educated at Dorpat who gave origin to modern metallurgy; and the American Arthur Amos Noyes (1866–1936), founder of Caltech and of the Chemical Abstracts; and Willis Rodney Whitney (1868–1958), creator of the electrochemical theory of corrosion and later director of General Electric.

Ostwald published during his lifetime as many as 45 books, among them the *Lehrbuch der Allgemeinen Chemie* (1885–1887) and the *Grundriss der Allgemeinen Chemie* (1889); more than 500 scientific papers; and about 5,000 reviews and reports. In addition, he was editor of six scientific journals, and in 1889 he organized the reprinting of a large series of papers of historical interest, the famous *Klassiker der exakten Wissenschaften*, of which as many as 250 volumes were published.

The foundation in 1887 – in collaboration with van’t Hoff – of the *Zeitschrift für physikalische Chemie*, first true journal of chemical physics that he edited until 1922, rapidly made him one of the key masters of the new discipline.

In 1902, he founded the *Annalen der Naturphilosophie* and in 1894 the *Deutsche Elektrochemische Gesellschaft*, the German society of electrochemistry that in 1902 transformed into the *Deutsche Bunsen-Gesellschaft für angewandte physikalische Chemie,* one of the most important European scientific societies.

In 1875, he started his experimental activity by measuring the variation of the physical parameters in chemical reactions that for several years he combined with the study of affinity, a vague expression representing the tendency of atoms to join and to react, at that time a problem central to all chemical theories.

Ostwald succeeded in coordinating in a single general framework several different ideas and measurements used to rationalize affinity (Ostwald 1880), taking up the research line of Julius Thomsen, but exploiting a different technique – that of measuring volume variations in chemical reactions that he considered simpler and more exact than calorimetry. The work object of his Ph.D. thesis in 1880 was based on the comparative study of the volume variation of couples of acid–base reactions in dilute solutions (Ostwald 1878), with a common component. If A_1 and A_2 are two acids and B is a base, the mixture of 1 L of acid A_1 with 1 L of solution of base B does not give as a result 2 L of solution of the compound A_1B, but a total volume slightly different by an amount v_1. In the same way, the mixture of 1 L of solution of acid A_2 with 1 L of solution of base B will give rise to a total volume differing from 2 L by the amount v_2. Finally, the mixture of 1 L of the A_1B compound with 1 L of solution of A_2 will not give as a result 2 L of mixture, since in the solution equilibrium takes place between A_1B, A_2B and the fractions of A_1 and A_2 free acids. The volume difference in this case furnishes an exact measure of how much of the A_1B compound has been transformed into A_2B.

At the end of the 1870s, he had already obtained significant results measuring the volume variation and other physical quantities in reactions and showing that these were in agreement with the mass action law formulated earlier by Peter Guldberg and Cato Waage. It was actually only, thanks to the citing of the papers of the two Norwegians by Ostwald, in 1875 that their law, practically ignored for more than 15 years, became known all around the world.

A decisive turn in the scientific activity of Ostwald began with the publication in 1884 of the Ph.D. thesis of Arrhenius discussing the development of the theory of electrolytic dissociation. Oswald realized right away the importance of the theory, realizing that it presented the possibility of using conductivity measurements to quantify chemical affinity in acid–base reactions. In the summer of 1884, he went to Sweden to meet Arrhenius and the other Scandinavian chemists Guldberg, Waage, and Thomsen, owing to his interest in their works.

In the meantime, van’t Hoff had deduced the law of mass action from basic thermodynamics principles and had shown that molecules in solution behaved as if they were in the gas phase. At first, the contribution of Ostwald to the dissociation theory was only to clarify and improve the ideas of van’t Hoff and Arrhenius. In 1887, however, he made a fundamental contribution with his law of dilution that connects the equilibrium constant to the degree of dissociation of electrolytes (Ostwald 1887). Starting from the Arrhenius finding that at infinite dilution the conductibilities of all acids are identical, Ostwald realized that dilute solutions of electrolytes behave as do the ideal gases, as he clearly stated in his famous paper of 1888 (Ostwald 1888):

> The researches of van't Hoff, Planck, and Arrhenius on dilute solutions have in recent times led to the recognition of a complete analogy of these with gases. One of the most valuable advances of these studies is that the compounds usually spoken of as held together by the strongest affinities, such as, for example, potassium chloride, hydrogen chloride, or potassium hydroxide, must actually be regarded in dilute solutions as very largely dissociated.

Ostwald also proved the importance of applying the mass action law to these solutions (Partington 1964). For a generic dissociation reaction of a molecule HA:

$$\underset{(1-\alpha)/v}{\mathrm{HA}} \rightleftarrows \underset{\alpha/v}{\mathrm{H}^+} + \underset{\alpha/v}{\mathrm{A}^-}$$

if one denotes with v the volume in liters of the solution containing one mole of solute, i.e., the inverse of the concentration c and with α the degree of dissociation, then the concentration of nondissociated molecules HA will be equal to $(1 - \alpha)/v$, whereas the concentration of dissociated particles H^+ and A^- will be equal to $2\alpha/v$ and, according to the mass action law, the equilibrium constant will be equal to

$$K = \frac{[\mathrm{H}^+] \cdot [\mathrm{A}^-]}{[\mathrm{HA}]} = \frac{\alpha^2}{v^2} \frac{v}{(1-\alpha)} = \frac{\alpha^2}{v(1-\alpha)}$$

Expressing the degree of dissociation as a function of the limiting Kohlrausch conductibility $\alpha = \Lambda/\Lambda_0$, this equation yields

$$K = \frac{\Lambda^2}{v\Lambda_0(\Lambda_0 - \Lambda)}$$

which is known as Ostwald's dilution law that allows one to compute the equilibrium constant from conductivity measurements. Ostwald and coworkers showed that hundreds of solutions of organic acids and bases obey the dilution law, confirming the validity of the ionic theory. Ostwald dilution law, the weak point of which was that it only holds for weak acids and bases, had a great number of applications (Ostwald 1889). Ostwald himself realized that the equilibrium constant K could be utilized to measure the strength of acids and bases. In the case of pure water, weakly dissociated,

$$\mathrm{H_2O} \rightleftarrows \mathrm{H}^+ + \mathrm{OH}^-,$$

the action of mass law reduces to $K = [\mathrm{H}^+]\ [\mathrm{OH}^-]$ since the concentration of water molecules is constant. From conductivity measurements, the value of K, known as the ionic product of water, was found to be equal to 10^{-14} $(\text{mol/L})^2$, and from this one obtains a value of 10^{-7} mol/L for the concentration of hydrogen ions in pure water (Ostwald and Nernst 1889).

Several chemists of the time proposed that the concentration of hydrogen ions in solution could be used as an indicator of the strength of acids and bases.

In 1909, the Danish biochemist Soren Sørensen (1868–1939), who for 8 years had been a director at the chemical laboratories of the firm Carlsberg, one of the most important companies for the production of beer, pointed out in a paper in a biochemistry journal (Sørensen 1909) that the quantity of an acid used expressed in moles/L did not correctly represent the acidity of the solution owing to chemical interactions with other chemical species present. Sørensen suggested instead that the degree of acidity should be measured by the exponent of the ionic concentration and proposed a scale that he called pH, from the French *pouvoir hydrogéne*. The pH scale soon became very useful for biochemists and analytical chemists, pH = 7 meaning that a solution was neutral, whereas lower or higher values indicated acidity or basicity, respectively.

Ostwald was also interested in thermodynamics and thermochemistry. In 1892, he realized the importance of Willard Gibbs' papers and the difficulties that the European chemists had in following the complex mathematical treatment and decided to make them accessible, translating them into German, simplifying the mathematical formalism, and reformulating the concepts in simpler forms (Ostwald 1892).

In the 1890s, Ostwald concentrated his efforts completely on the theoretical and philosophical problems of energy, convinced that matter was only a mirage created in our minds to embrace the energy activity.

For him, atoms and molecules were only symbols of statistical regularities, being convinced that the deep truths of science should be expressed only in terms of energy; for this reason he always objected to the atomic theory. Only in 1909, after having evaluated Perrin's experiments on Brownian motion, did he reluctantly accept the existence of atoms.

Ostwald received honors, awards, and honorary doctorates from more than 60 universities throughout the world and in 1909 the Nobel Prize for chemistry for his works on catalysis and reaction rates.

After his retirement from academic life, he dedicated himself to intense philosophical, political, and social activity aimed at research for peace in the world and to a better understanding between countries. He was also interested in educational reforms and in monism and tried without success to promote a new universal language "Ido," a new version of Esperanto. Outbreak of the First World War in 1914 dampened his dreams of great international collaboration. A confirmed patriot, but not a militarist, he vainly hoped for a rapid and rightful peace. Criticized by his compatriots for lack of enthusiasm for the actions of his country and by his international colleagues for not having condemned the war, he left active politics and concentrated on the study of colors and speculating on esthetic and philosophical problems.

The other father of electrochemistry was the Swede Svante Arrhenius (1859–1927) who developed the theory of electrolytic dissociation in solution. Enrolled at the Uppsala University in 1876, he started to study chemistry under the supervision of Per Cleve, the chemist who isolated holmium and thulium in 1879. Experimental teaching at Uppsala was not among the best and in 1881 Svante decided to move for a time to Stockholm to work with Eric Edlung (1819–1888) of the Swedish Academy of Sciences to measure electromotive forces. At Stockholm, he started his Ph.D. work which he continued after returning to Uppsala in 1884, without much success. The thesis project of Arrhenius, *Recherches sur la conductibilité galvanique des électrolytes* (Arrhenius 1884), was to determine the molecular weight of nonelectrolytes such as cane sugar, measuring the decrease of electrical conductivity of mixed solutions with electrolytes of known conductivity. Arrhenius did not succeed in solving the problem experimentally and was only able to prove that the molar conductivity increased as the concentration decreased, a result that only confirmed those obtained previously by Kohlrausch. Instead, it was the theoretical content of the second part of his thesis entitled *Théorie chimique des electrolytes* that assured his success.

Arrhenius concluded that the only way to explain his results and those of Kohlrausch was to assume that the electrolytes in solutions were a mixture of "complex" inactive molecules in dynamic equilibrium that did not conduct the current and of "active" parts that were responsible for conduction. As the dilution increased so did the number of dissociated molecules. Very probably, Arrhenius was convinced of the theory developed by Mendeleev (Brock 1993) that hydrates involving particles of solute and of water were formed and for this reason did not use the term "ion" at this stage.

It was only in 1887 that Arrhenius completed the development of his theory in terms of dissociation into positive and negative ions. The theory was first explained in a letter to his friend van't Hoff and then published (Arrhenius 1887) with Ostwald's support, receiving its definitive acceptance in 1903 with the speech of Arrhenius at Stockholm during the award of the Nobel Prize.

Arrhenius' thesis was not received with favor by the committee of the science faculty of the University of Uppsala which approved it with only a low vote. According to the tradition of Uppsala University, Arrhenius sent a copy of the thesis to the most renowned electrochemists of the time, among them Ostwald and van't Hoff. Happily for him, Otto Pettersson, professor of chemistry at the Högskola of Stockholm, defended the originality of the thesis and Ostwald, who had a preeminent position in European chemistry, was so enthusiastic that he even went to Uppsala to meet the young author and convince him to follow him to Riga, offering him the position of *Privatdozent* for the years 1884–1886. Ostwald's offer caused sufficient embarrassment to the scientific community of Uppsala which eventually saved face by offering to Arrhenius a chair of chemical physics, the first created in Sweden, at the end of 1884. Thanks to Edlund's influence, the Swedish Academy of Sciences awarded him a 5-year fellowship, enabling him to work with Ostwald in Riga in 1886, with Kohlrausch in Wurzburg, with Boltzmann in Graz in 1887, and with van't Hoff at Amsterdam in 1888.

In 1891, Arrhenius became teacher of physics at the Högskola of Stockholm, after having refused a position of professor at the University of Giessen. During this period, he became interested in the production of ions in flames (Arrhenius 1891). In 1895, he was made professor and in 1905, after receiving the Nobel Prize for chemistry, he became director of the Nobel Institute of Chemical Physics of Stockholm, inaugurated in 1909. In 1889, Arrhenius studied the inversion of cane sugar induced by weak acids, a process investigated before by Ostwald in 1884 (Ostwald 1884, 1885) and confirmed Ostwald's equation of reaction rates that since then has improperly been called the Arrhenius equation.

Arrhenius published two treatises on electrochemistry – the *Lärobok i teoretisk elektrokemi* (treatise of theoretical electrochemistry) in 1900 and *Theorien der Chemie* (theory of chemistry) in 1906 – and became interested in several other fields of science such as geophysics, meteorology, astronomy, and cosmology (Arrhenius 1903), developing theories on the influence of carbonic anhydride (Arrhenius 1896) in the atmosphere and on the possibility that the radiation pressure could be responsible for the dispersion of living spores in the universe (panspermia).

The electrolytic dissociation theory did not have an easy life, disputed between supporters and adversaries, both with valid arguments. The theory explained well in an intuitive and simple manner the existence of a dynamic equilibrium, controlled by the mass action law, between dissociated molecules and ions, electrical conduction in the solutions, and anomalies of the colligative properties of electrolytes. Strangely, however, it worked well for weak electrolytes and high dilutions, and worst for strong electrolytes and higher concentrations. In addition, it presented a conceptual difficulty that left many chemists doubtful of the solidity of its theoretical grounds. It was in fact difficult to accept the idea that, in a solution, positive and negative ions could freely coexist, unaffected by each other, when it was well known that in crystalline solids these ions formed stable and long-lasting structures with strong ionic bonds.

Additional political and academic difficulties added to those of a purely technical nature. Both in Germany and France, organic chemistry had seen a century of great splendor and it was difficult to accept that chemical physics could assert its authority as the only science able to explain what was happening in the test tubes and flasks of organic chemists. Furthermore, ionic theory was a typical outcome of German culture and after the Franco-Prussian war it received little support in the French-speaking world. On the other hand, different ideas on the interaction of solute with solvent molecules had arisen and these did not encourage the idea of ionization. In Russia, for instance, Mendeleev, the country's most influential and respected chemist, had already developed in 1865 his theory of hydrates that explained the anomalies of the colligative properties as due to the formation of hydrate structures as a function of temperature (Mendeleev 1877).

In England, Henry Edward Armstrong, supporter of the theory of residual affinities, thought that these residual affinities would associate the solute molecules to those of the solvent and explained the anomalies in the colligative properties of electrolytes as due to the formation of a connective network among water molecules caused by residual affinities.

The antipathy that Armstrong showed for the new chemical physicists is testified by his writing (Armstrong 1936):

> . . .people without knowledge of the laboratory arts and with sufficient mathematics at their command to be led astray by curvilinear agreements; without the ability to criticise, still less of giving any chemical interpretation. The fact is, the physical chemists never use their eyes and are most lamentably lacking in chemical culture. It is essential to cast out from our midst, root and branch, this physical element and return to our laboratories.

The eccentric Spencer Umfreville Pickering (1858–1920), for some time professor of chemistry at the Bedford College and since 1887 owner of a private laboratory in London, was also convinced that in electrolytic solutions the dissociation in ions did not really happen and that the observed anomalies for osmotic pressure and colligative properties of solutions of electrolytes were due to residual affinities that connected the solute and solvent molecules. Pickering is known for the discovery of the stabilization of emulsions by small particles.

The reception of chemical physics was different in American universities, which were undergoing great expansion and were ready to accept promising young scientists from Ostwald's laboratory at Leipzig.

Josiah Willard Gibbs and the school that he created at Yale were in favor of the development of chemical physics. Among the young people from Ostwald's laboratory, Louis Kahlenberg (1870–1941), professor of chemistry at the University of Wisconsin, was one of the few who, having departed from Leipzig as a convinced supporter of the ionic theory, rapidly became an active opponent. In 1901, Kahlenberg measured the dielectric constant of liquid cyanidric acid and found that, although higher than that of water, it was less effective in favoring electrolytic dissociation. This result was in contrast to those previously obtained by Nernst and Thomson showing that the increase in the dielectric constant favored dissociation. Kahlenberg, having realized that nonaqueous solvents also conducted electricity, started a long-term research project aimed at measuring the conductivity and the colligative properties of nonaqueous solutions (Kahlenberg 1902). He collected a series of "anomalies" published in articles in the *Journal of Physical Chemistry* that he considered countered the ionic theory, despite Ostwald clearly stating in 1899 that the ionic theory applied only to solutions (Ostwald 1899). Kahlenberg's anomalies showed that conductivity variations with concentration did not follow the mass action law and thus the role of the solvent needed to be taken into account in the ionic theory. Kahlenberg's ideas did not, however, find favor in the American electrochemical community, owing essentially to the strong support that the ionic theory had received from Noyes and Lewis, although they stimulated research on solutions of strong electrolytes and of inter-ionic interactions. In 1909, the Dane Niels Bjerrum (1879–1958) presented at a meeting held in London a report (Bjerrum 1909) on the spectroscopic investigation of chromium chloride, nitrate, and sulfate at different concentrations in aqueous solutions. Bjerrum proved that, since light absorption did not change with concentration, these salts had to be completely dissociated in solution, even at high concentration, and therefore the mass action law could not be applied in this case since there was no dynamic equilibrium. The conductivity variations and the decrease of the freezing point were therefore due to inter-ionic forces. Bjerrum's paper infuriated Arrhenius who considered any small revision of his theory as a personal insult. After a few years, however, Bjerrum's conclusions received unquestionable confirmation from x-ray analysis which proved that ions already existed in ionic crystals as independent entities.

3.2 Solutions

Solutions were always important to handle chemical compounds, especially when the conduction of current was important such as in electrochemical processes.

In the Middle Ages, the only solvent used by the alchemists and the "new" chemists was water. The dissolution of a chemical compound in water was for the medieval alchemists a way of respecting the will of Nature that all matter should be transformed in water, as maintained at the end of the sixteenth century by the Dutchman Johannes Isaac Hollandus in his treatise *De Lapide Philosophorum*. Hollandus's ideas agreed with those of van Helmont that all substances were obtainable from water and of Boyle who in the "Sceptical Chymist" wrote that it was possible to transform water into all other elements. The laboratory experience of medieval alchemists was condensed in the sentence *Corpora non agunt nisi soluta* (substances do not act if not dissolved) or in the more specific one *Salia non agunt nisi dissoluta, nec agunt si dissoluta nimis* (salts do not act if not dissolved and if not very diluted). Alchemists had also elaborated a series of practical rules derived from laboratory practice. A well-known rule, going back to medieval times, was expounded in the sentence *Similia similibus solvuntur* (similar substances will dissolve similar substances) that, in terms of the affinity theory, corresponds to the fact that the more similar the particles of the solvent to those of the solute, the greater the possibility that these could be dissolved.

In the search for solvents suitable to dissolve chemical compounds, the alchemist's main problem became that of discovering an ideal solvent, capable of dissolving everything. The existence of this ideal solvent, *summus atque felicissimus salium* (Porto 2002), was assumed in the sixteenth century by Paracelsus, who even invented the name *alkahest*, a name perhaps derived from *alkali est* (it is an alkali) or perhaps even from the German *al-geist* (all-spirit). However, Paracelsus never described the chemical composition of the alkahest. van Helmont, instead, said that he had truly obtained it and that it was a liquid resembling water so he suggested the name "ignisaqua." The liquid that van Helmont mentioned was probably a concentrated solution of caustic potash in alcohol, know to alchemists as *sal alkali*. Alkahest was considered the universal solvent par excellence and the alchemists, followers of Paracelsus, tried to outdo each other with their preparations, despite Johann Kunckel having ridiculed its existence by stressing that a universal solvent would first of all dissolve the receiver in which it was contained.

The alchemic dream of the alkahest even outlived the scientific revolution, entering the world's literature. In the Comédie humaine, Honoré de Balzac tells in *La recherche de l'absolu ou de l'alkahest* the tragic history of Balthazar Claës living at Douai in Flanders. A pupil of Lavoisier, after a meeting with a Polish soldier who told him of the alchemic dream, he decided to hide himself in his laboratory, quitting his family and squandering his fortune in research of the absolute, basic principle of the Creation.

For some time even the dissolution of a metal in an acid was considered as a type of solution, even if it was evident that it was fundamentally different from solution of a salt in water. The capability of acids to act as solvents of metals was explained assuming that the acid particles had sharp points that allowed them to trickle between those of the metal, separating them through violent pushes. These sharp points were even considered as responsible for the acid taste.

The first clear classification of the nature of solutions, separating the solution process from the dissolution process, appeared in the 1789 Lavoisier *Traité élémentaire de Chimie*. According to Lavoisier, in solutions of salts the salt particles were simply separated one from another but neither the salt nor the water was decomposed and both could be recuperated in the same amounts as before. The same was true for solutions of resin in alcohol or in other solvents.

In contrast, in the dissolution of a metal in an acid, a true decomposition of both acid and metal took place and neither of the two substances preserved its initial state; the metal was transformed into an oxide while a gaseous substance was produced. Dissolution was therefore a chemical transformation, whereas solution was a purely physical process.

A different distinction, strictly bound to the nature of electrochemical processes, was proposed by Theodor von Grotthuss at the beginning of the nineteenth century. For him, solutions and dissolutions differed because a solution was the conversion of a solid or a liquid into a new liquid, not separable with electricity into the original components. Dissolution was instead the conversion of a solid or a liquid into a new liquid, electrically decomposable into its elements (examples: acids and bases). Still different was the position of Berzelius, for whom a solution differed from a chemical process in that it preserves the original electrical charge distribution. The dissolved substance was, according to him, more active in a solution thanks not to a specific variation of affinity but preserved electrical differences between the two partners.

The alchemist speculations on solutions concerned the modus operandi (behavior) of the solvents rather than their nature. The most diffused opinion, developed within the framework of the corpuscular theory, was that the solute particles simply entered the pores or interstices existing in the solvent, an idea derived from Plato's Timaeus and taken up later by Pierre Gassendi. Since the salt particles were considered as small cubes reproducing the external form of the substances, it was necessary to assume that in water there were pores with a cubic shape to host the small salt mini-cubes. When all water pores were filled, the solution was saturated and no more salt could be dissolved in it.

Since, however, alum possessed an octahedral crystalline structure it was evident that water should also contain pores of this shape that only the alum crystallites and not those of the common salt could enter. The extension of this theory to all possible shapes of solute particles obviously presented too many difficulties and required too many ad hoc hypotheses to be easily accepted.

The development of a new theory of solution on a completely different basis started with Newton who extended to solutions the idea of attractive and repulsive forces. Newton supposed that the universal attraction force acting among celestial bodies was also responsible for the interaction between minute particles of different substances; a salt dissolved in water because the salt particles exerted on water particles an attractive force stronger than on other salt particles. When a solid was dissolved in a liquid it distributed throughout the whole volume of the liquid owing to the repulsive forces between the solute particles that tried to move away from each other while being attracted by those of the solvent.

This concept was taken up again by Herman Boerhaave who, in *De Artis Theoria*, went so far as to state that the action was reciprocal in the sense that the solute also dissolved the solvent and that the particles of solvent and solute were bound together to form a new homogeneous substance (Boerhaave 1732):

> post solutionem peractam, particulae solventes et solutae denuo se affinitate suae naturae colligant in corpora homogenea[1]

In other words, the nature of both substances changed since the particles' extension was smaller than their *minima naturalia*.

Georges Louis Leclerc, Count of Buffon, connected Newton attraction and repulsion forces between particles to their shape in solution. The form of the solvent and solute particles was, according to him, particularly relevant, since they were in close contact, in contrast with the attraction between celestial bodies, so far apart that their shapes had no importance. Johan Gottschalk Wallerius (1776) and Martin Heinrich Klaproth (1792–1793) were convinced that a solution was the result of a chemical affinity between solvent and solute and that the attraction between their particles was greater than the "cohesion" between particles of the same substance.

The ideas of Claude-Louis Berthollet on the composition of solutions, dictated by his polemics with Proust relative to the law of the definite proportions, were different again. In his 1803 book *Essai de Statique Chimique*, Berthollet called all stable compounds with a fixed composition "combinations" and those less stable with a variable composition "dissolutions" (Berthollet 1803). Even after having accepted the validity of the law of definite proportions, he insisted in distinguishing between chemical combinations always occurring in definite proportions and solutions occurring instead in any possible proportion, at least up to a given limit. According to him, a solute could dissolve in a solvent only if the attraction forces between them could overcome the cohesion force of the solute, and therefore this

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[1] Once the solution had taken place, the solvent and solute particles, due to the nature of their affinity, were connected again in a homogeneous body.

had to be considered to be a true chemical process. The true difference between a compound and a solution was to be found only in the strength of the union of the parts.

The idea that solutions were true chemical compounds was shared by several members of the nineteenth-century chemical community such as Thomas Thomson and Herman Kopp, who proposed interesting variations to Berthollet's position. Thomson, for instance, distinguished between solids which dissolved in liquids and becoming liquids themselves and solids which instead combined with part of the solvent while remaining in hydrated solid forms. Kopp distinguished between compounds obeying the law of definite proportions and compounds with variable amounts of constituents.

The beginning of the nineteenth century witnessed intense research activity on the chemical physics of solutions, ranging from the study of the properties of electrolytes, discussed in detail in the next section, to the examination of the colligative properties of solutions depending only on temperature, pressure, and concentration and not on chemical composition.

The dependence on temperature of the colligative properties of solutions, in particular their freezing points and vapor tensions, proved to be very important to furnish precise methods of determining the molecular weight of chemical compounds. It had been known for a long time that, by dissolving chemical substances in water, their freezing point could be decreased and this gave rise to the production of frigorific mixture for the preparation of ice creams.

The Greeks and Romans used minced ice granules with honey or fruit juice. Sherbets (*sharbat*, fresh drink) were probably invented by the Arabs and later taken up by Sicilians and Neapolitans who exported them to Europe. In the sixteenth century, a courtesan called Ruggeri at the Court of Catherina of the Medicis prepared an ice cream made of water and perfumed ice, and the architect Bernardo Buontalenti (1531–1608) invented an ice cream made of ice and zabaglione (a *dessert made of egg yolks, sugar, and marsala*). It was, however, the Sicilian Francesco Procopio dei Coltelli who first developed the industry and commerce of ice creams, opening the *Café Procope* in Paris in 1686, where ice creams were already being sold around the end of the sixteenth century.

The first description of a freezing mixture made with ice, salt, and water goes back to the writings of the Islamic physician Ibn Abu Usaybi'a (1203–1270) and the technique probably reached Europe through Spain during the Arab domination. Freezing mixtures were already known in the sixteenth century and the Italian humanist and philosopher Gian Battista della Porta (1535–1615) mentioned them in his treatise *Magiae naturalis sive de miraculis rerum naturalium* of 1558. In 1724, Gabriel Daniel Fahrenheit (1686–1736), a German instrument-maker living in the Netherlands, found that a mixture in equal parts of water, ice, and Ammonium Chloride salt melts at −32°C, a temperature that he selected as the zero of a new temperature scale that bears his name (Fahrenheit 1724). In addition, in 1788 Charles Blagden (1748–1820), assistant and coworker of Cavendish, found that the melting point of water decreases with dissolved chemical substances and that the decrease is proportional to the quantity of dissolved substance (Blagden 1788).

Blagden gave a mathematical form to his numerous measurements, showing that the ratio between the decrease C of the freezing point and the quantity P of dissolved substances was expressed by the equation

$$\frac{C}{P} = K$$

where K is a constant specific to any kind of solute (Blagden law).

Research on the decrease of the freezing point of aqueous solutions merged with that on the variation of the density of water with temperature and the extension to solutions. In 1805, the Scot Thomas Charles Hope (1766–1844) showed that water density had a maximum at about 4°C (Hope 1805), and in a short while the Belgian César Mansuète Despretz (1789–1863), professor of physics in Paris, realized that the same phenomenon occurred with solutions, which the Paduan Francesco Rossetti (1833–1885) was able to connect with that of the freezing point decrease (Rossetti 1869).

The question was reconsidered by the French-Swiss Louis de Coppet (1841–1911) who in 1871 proved that solutions with the same freezing temperature had equal concentrations of dissolved substances (de Coppet 1872).

Frenchman François-Marie Raoult (1830–1901) conducted more than 20 years of research on the physical properties of solutions, and in particular on cryoscopy (from the Greek κρυοσ, ice, and σκοπεω, to examine). He started by studying electrical processes and then considered strictly chemical problems. From 1878 onward he studied the colligative properties of solutions, properties that depend only on the number and not on the chemical composition of dissolved particles. In the same year he published his first paper on the depression of the freezing point of solvents as a function of the concentration of the solutes (Raoult 1887). In this field he published about 60 papers with freezing temperature tables of a large number of solutions that made him known all over Europe. At first he attributed the phenomenon to the effect of the affinity of the solutes for water, but soon, working with organic solvents such as benzene and acetic acid, he realized that a simple relationship existed between the concentration of the solute and the decrease of the freezing point of the solvent. In 1882, he proposed (Raoult 1882) the *loi générale de la congélation* which establishes that if a molecule of a compound is dissolved in 100 molecules of a solvent, the freezing point decreases by 0.63°C:

> Il est donc permis de dire, dès à présent: Dans une multitude de cas, l'abaissement du point de congélation d'un dissolvant ne dépend que du rapport entre le nombres de molécules du corps dissous et du dissolvant; il est indépendant de la nature, du nombre, de l'arrangement des atomes qui composent les molécules dissoutes

Raoult's work had important implications for the extension of the theory of solutions to chemical kinetics and electrochemistry. A surprising result was that the depression of the freezing point of water with inorganic salts was almost double that of the same concentration with organic substances. This result was interpreted by Raoult as distinguishing between physical and chemical molecules, namely, between the molecules and the items into which these were dissociated in solution.

De Coppet had also realized that the freezing point depression of a solvent was related to the molecular weight of the solute, but he did not reach the conclusions that Raoult had, thereby transforming cryoscopy measurements into a convenient method for the determination of molecular weights. At that time the definition of atomic and molecular weights was still a source of confusion. The chemical formula H_2O for water implied an atomic weight of 16 for oxygen, but leading chemists like Berthelot continued to maintain the HO formula, leading to an atomic weight of 8 for oxygen. Raoult's measurements definitely showed that the atomic weight of oxygen was 16.

In parallel with cryoscopy, Raoult worked on another colligative phenomenon, the variation of the vapor tension of solvents. He found that for diluted solutions, this depression is proportional to the solute concentration and in 1887 calculated (Raoult 1887) the reduction of the vapor tension K due to a molecule of substance dissolved in 100 g of liquid from the relationship

$$K = \frac{f - f'}{fP} M$$

where f is the vapor tension of the pure solvent and f' that of the solution, M the molecular weight of the solute, and P the weight of solute dissolved in 100 g of solvent. Similar results had previously been obtained by others such as Adolph Wüllner (1835–1908) and Gustav Tammann (1861–1938).

Vapor pressure measurement became a very precise method thanks to the invention made by Ernst Otto Beckmann (1853–1923), a pupil of Kolbe and Wislicenus, of a very high precision thermometer (Beckmann 1888) that made it possible to measure temperature differences of about 0.001°C. Beckman was an organic chemist who, after having discovered the acid catalyzed rearrangement of an oxime to an amide (Beckmann 1886), investigated the determination of molecular weights to evaluate the dimension of the oximes he had synthesized. First, he used Raoult's law of vapor tension depression, but soon realized that it was simpler and more precise to measure boiling point increase, giving rise to the birth of ebullioscopy, a technique that had developed parallel to cryoscopy for molecular weight determinations. The mathematician William Esson (1838–1916), a coworker of Harcourt, interpreted Harcourt's kinetic data in terms of differential equations not too different from those used today (Harcourt and Esson 1867). In 1878, John J. Hood found empirically that the reaction kinetics of oxidation of ferrous sulfate with potassium chlorate catalyzed by sulfuric acid is regulated by an exponential law (Hood 1878) and only a few years later Max Bodenstein integrated these results with those concerning the reaction between hydrogen and iodine (Bodenstein 1894, 1897, 1899).

Of equal interest was the research at the end of the eighteenth century concerning another colligative property of solutions, the osmotic pressure, namely, the hydrostatic pressure produced by a solution in contact with the pure solvent through a semipermeable membrane (which allows only the solvent molecules to pass through). Osmotic pressure was discovered in 1748 as the result of a curious experiment of the French clergyman known as the Abbé Jean Antoine Nollet (1700–1770), tutor of natural philosophy to King Louis XV and a strong adversary of Franklin's electric fluid theory. Nollet immersed in water in a container a bottle filled with alcohol sealed with a pig's bladder; after some hours he saw that the bladder had expanded inside the water container, showing that some water had entered the bottle (Nollet 1748). By switching the water with alcohol, the opposite reaction occurred and the bladder contracted into the water bottle, showing this time that some water had left the bottle and entered the alcohol in the container. It was easy for Nollet to deduce that the bladder was more permeable to water than to alcohol. Nollet's experiment remained a scientific curiosity for a while until it was taken up by the French botanist René Joachim Henri Dutrochet (1776–1847), a descendant of a noble family which had fallen out of favor during the French revolution, who, by investigating the motion of liquids in plants and diffusion through semipermeable membranes, gave full credence to the study of osmotic pressure. Dutrochet built an osmometer, a device to measure osmotic pressure quantitatively, and studied the transport of water and of solutions through animal membranes (bladders and pigs' intestine walls) or in vegetable tissues. He was also one of the first to understand that cellules were minute bags of liquid (Dutrochet 1837) and to appreciate their importance for the activity of living organisms. For the passage of liquids across cellular membranes he coined the words "endosmosis" and "exosmosis" (Dutrochet 1828), and since then the word osmosis has entered the scientific language.

Research on osmotic pressure became an important topic for botanists interested in the circulation of fluids in plants such as the Dutch Hugo de Vries (1848–1935) who studied plasmolysis in sugar beet, the Polish-German Moritz Traube (1826–1892), inventor in 1866 of a fragile chemical membrane permeable only to water, or the German Wilhelm Pfeffer (1845–1920) who, in order to measure osmotic pressure, built in 1887 a cell in which a porous septum held a semipermeable membrane made of copper ferrocyanide separating the solution from the pure solvent (Pfeffer 1887).

For some time, very few chemists were interested in osmotic pressure, among them Justus von Liebig, who showed interest in the subject in relation to his research of biological interest, and Thomas Graham, who had studied the diffusion of solutions as a function of concentration and molecular mass. Osmotic pressure thus remained of little interest until it attracted the attention of van't Hoff, the rising star of chemical physics. As all chemists of his time, van't Hoff was interested in measuring the affinity that appeared to be responsible for reactions among molecules, but was still not easily quantifiable and translatable in measurable quantities. An attempt to find a numerical value for a quantity somehow connected to affinity had been made in 1844 by Eilhard Mitscherlich (1794–1863), the discoverer of isomorphism, who, while working with Berzelius, became interested in the affinity problem. Mitscherlich attempted to measure the attractive force of hydration water in salts controlling the decrease of the vapor tension in these crystals. By introducing some crystals of Glauber salt ($Na_2SO_4{\cdot}10H_2O$) into the empty space on top of a barometer, he observed that the mercury height decreased by 5.45 mm with respect to pure water that produced a decrease of 8.72 mm. He thus deduced that the difference of 3.27 mm represented the affinity of sodium sulfate for hydration water, corresponding to a force of 12 g/cm^2 (Mitscherlich 1844). van't Hoff read Mitscherlich's paper and was impressed by the low value of the hydration force, believing that even the weakest chemical forces should have been much larger.

As he stated, one day in the streets of Amsterdam he met his friend Hugo de Vries who told him that his colleague Wilhelm Pfeffer, had observed a dependence of osmotic pressure on temperature, finding that each degree of temperature decrease reduced the osmotic pressure by about 1/270.

van't Hoff immediately realized the importance of osmotic pressure for the evaluation of chemical affinity and decided to use the kind of osmotic cell invented by Pfeffer to confirm his ideas. Using a diluted solution of cane sugar in water, van't Hoff proved that the attraction between water and sugar was more than 100 times stronger than that measured by Mitscherlich between sulfate and hydration water. From these measurements he deduced a result far more important and general, namely, that in diluted solutions the solute particles behave like particles of an ideal gas and therefore that osmotic pressure is linearly proportional to absolute temperature as is the pressure of an ideal gas. In 1886, van't Hoff published a new text in French entitled *l'Équilibre chimique dans* I'*État dilué gazeux ou dissous* that presented his ideas on the chemical physics of diluted solutions, establishing a perfect parallelism between ideal gases and diluted solutions in the form of the equation $\pi = \acute{\imath}cRT$ where π is the osmotic pressure, R the universal gas constant, T the absolute temperature, c the concentration, and í an empirical corrective coefficient. This equation, practically identical to the state equation of gases, $PV = nRT$, was perfectly valid (Van't Hoff 1887) for dilute solutions of organic compounds such as sugar with a numerical value of $\acute{\imath} = 1$. Determining í by different physical methods, such as the increase of boiling temperature or using Raoult's data on the decrease of freezing point, van't Hoff realized that for solutions of acids, bases, and inorganic salts, í assumed instead values close to 2. Van't Hoff did not present a valid explanation for the meaning of his empirical constant í in these cases. Only in 1887 did Arrhenius, with whom van't Hoff was in contact, suggest (Arrhenius 1887) that a value of í of the order of 2 was nothing other than proof of the fact that electrolytes were dissociated in solution and therefore that the concentration of solute particles was almost the double. van't Hoff accepted Arrhenius explanation with enthusiasm, reinterpreting his data in terms of dissociation in ions in a paper that he published in the same year with the favorable agreement of Ostwald (van't Hoff 1887).

The analogy between dilute solutions and ideal gases turned out to be very seminal for the extension of the second principle of thermodynamics to solutions (van't Hoff 1894). The parallelism allowed the full thermodynamical machinery developed for gases to be rapidly extended to solutions as well as the general relationships controlling the thermodynamic properties of diluted solutions to be found.

After the fundamental work of Gibbs on the thermodynamics of condensed systems and on chemical potentials, the application to solutions was effectively developed by the Americans John Kirkwood and Frank P. Buff in 1940–1960.

John Gamble Kirkwood (1907–1959) was a theoretical physicist who has made fundamental contributions to statistical mechanics and thermodynamics and to the theory of liquids. Kirkwood developed his treatment of the liquid state and of solutions in terms of very refined and elegant mathematics that makes use of the formalism of molecular distribution functions, today a normal component of physical-chemical research but very pioneering and of difficult application then. His most important contribution was to identify an intuitive technique of approximation that allowed the basic equations describing the structure and properties of liquid systems to be solved. In collaboration with Frank P. Buff (1924–2009), he published in 1951 a fundamental paper that represented the basis of all future developments (Kirkwood and Buff 1951).

3.3 The Debye–Hückel Theory

The beginning of the twentieth century saw a number of attempts to extend the validity of the ionic theory to strong electrolytes by developing either the treatment of the inter-ionic forces or the theory of the hydrates. The idea that nonideal behavior depended on long-range Coulombic interactions between ions was universally accepted but, owing to the complexity of the problem, an adequate theoretical treatment of these effects was still missing. Different attempts with scant results were made with more or less complex models such as that of William Sutherland (1859–1911), a Scot who had immigrated to Australia, author of a diffusion equation known as the Einstein–Sutherland equation, who in 1886 became interested in the interactions between molecules. In 1905, Sutherland wrote an obscure paper (Sutherland 1905) on inter-ionic forces starting from the assumption of complete dissociation of strong electrolytes. In addition, Englishman Samuel Roslington Milner (1875–1958) developed in a series of papers from 1912 to 1919 mathematical models of inter-ionic interactions between solute ions and solvent molecules (Milner 1919–1920). Another attempt to introduce inter-ionic forces in theory was made in 1918 by Jnanendra Chandra Ghosh (1893–1959), an attempt that after a brief initial success proved to be wrong and was rapidly forgotten (Chandra Ghosh 1918). In 1923, the treatment of inter-ionic interactions was, however, correctly resolved by Peter Debye (1884–1966) and his assistant Erich Hückel at the Eidgenössische Technische Hochschule of Zurich, who found a final solution to clarify the properties of strong electrolyte solutions, starting a new era for the study of electrochemistry.

The Debye–Hückel theory (Debye and Hückel 1923) also started from the idea that strong electrolytes were completely dissociated in solution. The tendency of ions to migrate and to give rise to an electric current was, however, counterbalanced by the electrostatic interactions between ions of opposite charge and between ions and solvent molecules, an effect that increased with solute concentration.

The basic idea of the theory was that, as a consequence of attraction between opposite charges, there were on average more ions of different than of the same sign surrounding an ion. Each ion was therefore surrounded by an atmosphere of charges of opposite sign that in the absence of an external field had central symmetry.

When, however, a current started to circulate in the solution and all positive ions moved in the direction of the negative pole and vice versa, each ion rebuilt an atmosphere of opposite sign in its motion, while that left behind slowly dissolved. Since the two processes were not instantaneous, namely, did not take place at the same time, the result was that an attractive force was exerted in the direction opposite to that of the ion motion that slowed it down.

The influence of the cloud of opposite charges on the velocity of an ion is called the relaxation effect. There is in addition a further factor opposed to ion movement, due to the fact that its ionic cloud tends to move in the direction opposite to that of the ion by consequence of the external field; this is called the electrophoretic effect since it is equivalent to that which opposes the motion of colloidal particles in an electric field. Finally, ion motion is also hindered by the viscosity of the medium, an effect controlled by Stokes' law and depending on viscosity and particle radius. The idea of the theory was that every ion creates a potential that exerts a Coulomb force on all ions in its neighborhood. This force decreases exponentially as the distance increases owing to the shielding effect of the surrounding ions. In order to obtain a reasonable expression for the potential, Debye and Hückel utilized a known theorem of electrostatics, analytically expressed by the Poisson equation that allows the variation in time of the electrostatic potential at any point of a system to be calculated as a function of the charge density at that point.

By solving Poisson's equation with the approximation that the disordered motion of the ions can be described as a diffuse density of charge around the central ion, they obtained for the average potential ψ the expression $\psi = \frac{e^{-\kappa r}}{r}$ where the shielding factor $\kappa = \sqrt{\frac{8\pi e^2}{DkT}\mu}$ depends on the dielectric constant D and on the ionic force μ that measures the total ionic concentration in solution.

A great success of the Debye–Hückel theory was to explain the behavior of strong electrolytes in diluted solutions and to prove the importance of ionic force in determining activity coefficients of electrolytes, namely, the effective concentrations of the species involved in liquid-phase reactions.

The theoretical previsions were, however, verified only for dilute solutions of salts and acids of univalent elements (HCl, NaCl, etc.) and became less and less valid as the electrolyte concentration increased.

In 1923, when the Debye–Hückel theory was published, Lars Onsager was still a student at the *Norges Tekniski Hoslashgskole* in Trondheim that he had joined in 1920. In 1925, he realized that molar conductivity values predicted by the Debye–Hückel theory were very different from those obtained experimentally and understood the reason for these differences. In the same year, after his graduation in technical engineering, Onsager accompanied his professor Johan Peter

Holtzmark in a trip to Denmark and Germany and eventually to Zurich, where he stayed for about 2 months. During this period, he had the opportunity to present his ideas on the theory of strong electrolytes directly to Debye. When he met Debye for the first time, he simply turned to him saying: "Professor Debye, your theory is wrong!" Debye, instead of being offended and without batting an eyelid, offered him a position of researcher at Zurich that Onsager accepted for 2 years.

Debye and Hückel had based their treatment on the idea that the electrostatic field due to an ion in motion in a solution was "shielded" by the atmosphere of opposite charges and that the effective shielding distance was inversely proportional to the square root of the ionic force. Their equation for the calculation of the molar conductibility of the form

$$\Lambda = \Lambda_0 + \Lambda_1\sqrt{c}$$

was formally correct but the computed values of Λ_1 differed appreciably from the observed ones. This result seemed strange to Onsager who believed that Debye and Hückel had correctly considered the presence of the electrophoretic and relaxation shielding effects.

In 1923, Onsager verified the consequences of the Debye–Hückel treatment, and in 1925, before visiting Debye, he had already found the reasons for the disagreement between observed and computed molar conductivity Λ. As he later wrote in 1968 (Onsager 1968):

> The relaxation effect ought to reduce the mobilities of anion and cation in equal proportion. Much to my surprise, the results of Debye and Hückel did not satisfy that relation, nor the requirement that wherever an ion of type A is 10 Å west of a B, there is a B 10 Å east of that A. Clearly something essential had been left out in the derivation of such unsymmetrical results.

Debye and Hückel had computed the conductivity Λ in the assumption that an ion moved along a straight line toward the pole of opposite sign among all the other ions in random Brownian motion in the field created by their charge distribution. Onsager realized that in order to obtain good agreement with experimental data, it was sufficient to eliminate the restriction that the central ion moved in a uniform motion, leaving it instead free to move randomly through the neighboring ions, under the effect of their presence and of the external field. Onsager developed his modification of the Debye–Hückel law in two famous papers known as the Onsager limiting law (Onsager 1926, 1927) and later in another significant paper in collaboration with his pupil Raymond Matthew Fuoss (Onsager and Fuoss 1932).

During 1955–1965, Onsager considered again the problem of the behavior of electrolytes in collaboration with his old student Raymond Fuoss (1905–1987) who, in 1995 had also obtained a position of professor at Yale. Together they reexamined the approximations of the Debye–Hückel–Onsager theory of 1927 and reformulated it in a series of highly sophisticated papers (Fuoss and Onsager 1955, 1958) without, however, reaching any truly innovative result.

3.4 Acids and Bases

The year 1923 was a year of grace for electrochemistry. Within a few months two independent theories relative to the electrochemical nature of acids and bases, albeit almost coincidental, were published to complete the framework of the study of electrochemical solutions supplied by the Debye–Hückel theory and by Onsager's modifications. The first among them was by the Dane Johannes Nicolaus Brønsted (1879–1947) who graduated in chemistry in 1903 at the University of Copenhagen and obtained his Ph.D. in 1908 with a thesis on the affinity of binary mixtures of sulfuric acid and water. In the same year, he became professor at the same university, beating in the competition another famous candidate, Niels Bjerrum, his inseparable colleague and friend.

Brønsted's theory of acids and bases (Brønsted 1923) defined an acid as a compound tending to give a proton and a base as a compound tending to acquire one.

This new idea explained all known experimental facts and allowed the concept of acid and base to be extended to compounds that could not previously be classified as such, for instance, water. New concepts such as those of acid and conjugated base or those of base and conjugated acid thereafter became integral parts of the electrochemical language.

A conjugated base was that part of a molecule of an acid remaining after having taken out a hydrogen atom (proton) whereas a conjugated acid was the molecule of a base that had accepted a proton:

$$\mathrm{HA} + \mathrm{OH}^- \rightleftarrows \underset{\text{basis}}{\mathrm{A}^-} + \underset{\text{acid}}{\mathrm{H_2O}}$$

Thanks to Brønsted's approach a new ion appeared in acid–base reactions, the hydronium ion H_3O^+, formed by the union of a hydrogen atom and a water molecule:

$$\mathrm{HA} + \mathrm{H_2O} \rightleftarrows \mathrm{H_3O^+} + \mathrm{A^-}$$

According to Brønsted, when a hydrogen atom is created, it is immediately attracted by a polar molecule of water, giving rise to a symmetrical structure with three hydrogen atoms around a central oxygen atom.

The second theory was developed in the same year (Lowry 1923) by the Englishman Thomas Martin Lowry (1874–1936), professor of chemical physics at the University of Cambridge. Starting from the study of the variations of the rotatory power of camphor derivatives produced by acid and base catalyzed reactions, he reached independently the same result, formulating a theory practically identical to that proposed by Brønsted.

These theoretical results were in a short time associated with important experimental developments that transformed electrochemical techniques into powerful analytical methods – polarography and electrophoresis.

Polarography was invented by Jaroslav Heyrovsky (1890–1967), born in Prague into a family of the university milieu. After having studied chemistry in his native town, Heyrovsky went to study at the University College of London from 1910 to 1914 where, in 1913, he obtained a bachelor degree under the supervision of Sir William Ramsay and, above all, of Frederick George Donnan (1870–1956), who encouraged the young Czech to take up the study of electrochemistry.

As a matter of fact, while Heyrovsky attended the University College laboratories, Donnan studied the equilibrium between two solutions of electrolytes separated by a semipermeable membrane that allowed only solute molecules to go through, thereby giving rise to a concentration difference that could be detected by measuring a potential difference between the two sides of the membrane (Donnan effect).

During the First World War, the young Heyrovsky worked as dispensing chemist and radiologist in a medical hospital, a situation which enabled him to continue to pursue his studies and to obtain his Ph.D. first in Prague in 1918 and then in London in 1921. He then started his academic carrier as assistant to Bohuslav Brauner in analytical chemistry and became associate professor in 1922 until in 1926 he held the first chair of chemical physics at the Carl I University in Prague. In 1922, he invented the polarograph and then concentrated his research activity on the development of polarography, a technique that became an important branch of electrochemistry when, in collaboration with his student Masuzo Shikata (1895–1964), he developed the automatic polarograph (Heyrovský and Shikata 1925). For this invention, Heyrovsky received the 1959 Nobel Prize for chemistry.

Polarography is an analytical technique based on the measurement of the electrical current flowing in a controlled voltage circuit made from a capillary dripping mercury droplets and a reference electrode immersed in an electrochemical solution.

The polarographic technique originated from a previous analytical method in which, for a given applied voltage at the electrodes, the mercury droplets falling from the capillary were counted in a definite time interval. The collected mercury droplets were accurately dried and weighted and the operation was repeated for different values of applied voltage. The mercury weights obtained were eventually reported in a graph as a function of the voltage. The innovative idea of Heyrovsky was that, instead of counting the mercury droplets, it was more convenient to measure the diffusion current flowing in the cell, proportional to the concentration of the chemical species present in solution. In this way, he obtained current–voltage curves for each concentration of the electrolyte.

Another important chemical physics technique connected with the motion of electric charges in liquids is electrophoresis which uses an electric field to move the charged molecules in the fluid. Particles with a positive charge are displaced toward the cathode (cataphoresis) and those with a negative charge toward the anode (anaphoresis).

The idea that it might be possible to displace electrically charged molecules, even of great dimensions, by means of an electric field was quite widespread in the first part of the twentieth century. Electrophoresis became an important analytical technique for the study and separation of proteins, thanks to the researches of the Swede Arne Wilhelm Kaurin Tiselius (1902–1971) born in Stockholm and educated at the University of Uppsala. An assistant in 1925 of Theodor Svedberg (1884–1971), he obtained his Ph.D. in chemistry in 1930 with a thesis on the electrophoresis of proteins (Tiselius 1930). An associate professor at the University of Uppsala, Tiselius became full professor and director of the institute in 1938. Under Tiselius' direction, the Uppsala Biochemistry Institute contributed to the development of a large number of important biochemical techniques such as electrophoresis, chromatography, gel filtration, etc. The Tiselius group also applied these techniques with great success to the study of molecules of very high molecular weight (Tiselius 1937), essentially enzymes and proteins (Tiselius 1939), but also polysaccharides and nucleic acids.

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