

AN OUTLINE OF THE HISTORICAL DEVELOPMENT
OF ELECTROCHEMISTRY a)

J. SIMÕES REDINHA

Departamento de Química, Universidade de Coimbra, 3000 Coimbra

Electrochemistry can be defined as the scientific branch which involves changes occurring in chemical systems due to the supply of electrical energy, or of chemical changes that are accompanied by the release of electrical energy.

As matter is constituted of particles with electrical charge, electrochemistry is a vast domain which is intimately related to practically all the areas of chemistry. The terms electroanalysis, electrocatalysis, organic electrosynthesis, photoelectrochemistry are examples of this. Also, there are no well-defined frontiers with other sciences, and important interdisciplinary areas have been established, such as bioelectrochemistry.

The large number of industrial processes which have an electrochemical basis strongly characterises it as an applied science. Without seeking to do so exhaustively, we can note some of the industrial applications. The production of metals (like aluminium, sodium, lithium, magnesium, zinc, and copper) of gases (like hydrogen, chlorine) of inorganic compounds (like the hydroxides of sodium and potassium, and sodium hypochlorite), of organic compounds (e.g. adiponitrile, tetraethyl lead, organophosphorous compounds) are counted as some of the most important products. The metallic coating of

a) Based on the invited lecture delivered at the Celebratory Session of 5th Anniversary of the Portuguese Electrochemical Society, Lisbon, 1989.

surfaces by electrodeposition (galvanoplasting) has been in use for a long time to modify the appearance, hardness, resistance to corrosion, of a large number of materials, is another expanding industry whose field has been broadened recently to include the manufacture of circuits intended for modern means of communication and computer technology. Alongside these processes, which are consumers of electrical energy, many on a large scale, there are electrochemical systems supplying energy and these are really quite important in the economy and day-to-day living. Batteries and accumulators are examples of these suppliers.

In this account we are presenting the most significant steps in the history of electrochemistry. It does not pretend to be a history, but simply a way to remember in a commemorative session like this, some aspects of the life of the science which is being honoured here today.

It is customary to refer the birth of electrochemistry to the studies of Galvani¹ which were carried out between 1780 and 1790. Luigi Galvani, professor of medicine at the University of Bologna, started investigating the action of an electrical current on muscle tissue. In the course of his experiments he noted that when a tissue preparation made from the muscles and nerve of a frog's leg was placed near a working electrostatic machine and was touched by a metal wire, a

muscular contraction was observed. Surprised by these observations, he carried out experiments under various conditions, in some of which the preparation was fixed between two wires made from different metals, iron and brass, and noted muscular contraction, just the same, as seen as the two wires touched each other, even though the electrostatic machine was not working.

Galvani attributed the effects observed to the discharge of an electricity inherent in the bodies of all living things, called animal



Dr. Luigi Galvani

electricity. The muscles and the nerve of the anatomical preparation of the frog behaved in the same way as the coatings of a Leyden jar (very popular at that time), resulting in the electrical discharge through the metal wire fixed in the tissue.

His work *De Viribus electricitatis in Motu Musculari Commentarius* was published in 1791 in the *Opuscula* of the Academy of Sciences and Arts of Bologna.²

This discovery caused a great deal of scientific and even popular interest, and the miraculous experiment with frogs was repeated everywhere. Popularity was an important factor for the continuity of the research, and perhaps because of this, various versions of the accidental nature of Galvani's discovery have been handed down to us.

One of the people who became interested in Galvani's results was the Professor of Physics at the University of Pavia, Alexander Volta³ who, in 1792, wrote to him with the intention of obtaining an interpretation of the origin of the current, but found the replay unsatisfactory. So he began to do some research in this area using different metals and tissues, not just those of frogs, but others animals. This led him to the conclusion that the electricity was

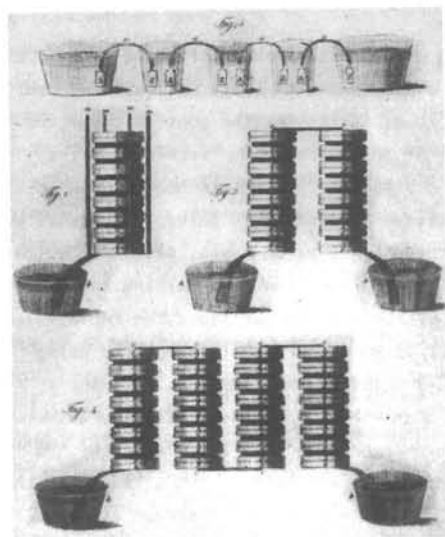
generated on the contact of the metals held by the tissue, and that the latter only served as an indicator of the existence of an electrical current. This interpretation was presented in two letters published in the *Philosophical Transactions* under the title *Account of some Discoveries made by Mr. Galvani of Bologna with Experiments and Observations on Them*.



A. VOLTA

The confirmation that the frog could be replaced by a piece of cloth or card soaked in a solution of salt must have led him to invent the first generator of electrical current of chemical origin. The first version was a "crown of cups" which was a battery of cells of silver and zinc dipped in salt water. This was

followed by another, shaped like a column, consisting of pairs of silver and zinc discs, arranged alternately with a disc of damp card or cloth between each couple. This model was more compact and occupied less space than the first one. In the figure some of the various versions suggested by Volta are shown.



VOLTA'S ELECTRIC BATTERY

Volta's battery, besides being of scientific interest in the manner of its invention, came to have a decisive role in the development of electrochemistry as a source of electric current for the research studies that followed. It differed from the friction machine in that it produced a more stable, high-intensity, low voltage current. This was, for about forty years, the only generator of electrical current used in electrochemical studies.

Volta went on to study the behaviour of electrical conductors which he classified into two groups. Good electrical conductors such as metals and carbon belonged to the first group, and solutions to the second.

Conductors in the first group were further arranged by him in a "series of tensions" according to the way in which the current passed from one of those placed higher in the order to one of the lower placed, when two of them were put in contact with a conductor from the second class, i.e. a solution.

Just after Volta established the electromotive series, Johann-Wilhelm Ritter,⁴ a member of the Munich Academy, showed that this agreed which one metal precipitated the others from the respective solutions. For example, zinc precipitated copper from a solution of the

latter, whilst copper, in turn, precipitated dissolved silver. The ordering was: first; zinc, followed by copper, and, last, silver.

Ostwald considered this work, which was given little prominence at the time, the first study in electrochemistry.

On 20th March 1800, Volta sent a letter to the President of the Royal Society in London, Sir Joseph Banks. In it he included the communication: *On the Electricity Excited by the Mere Contact of Conducting Substances of Different Kinds*. Banks showed the letter privately to Carlisle⁵ who discussed it with Nicholson,⁶ owner of a scientific journal, *Journal of Natural Philosophy, Chemistry and the Arts*, better known as *Nicholson's Journal*.

In May of that year these two researchers started a series of experiments with a battery built by the former. This led them to the correct formulation of the origin of voltaic electricity and to the demonstration of decomposition of water by the action of the electric current.

In the course of their experiments the two investigators showed that when a drop of water was placed on the contact of the metal wire and the battery's zinc disc, ensuring better electrical conduction, hydrogen was released. As a result of this observation, or perhaps because of the knowledge gained about the effect of electricity on water from work published in that journal, they applied the current supplied from the battery to two metals wires placed at the opposite ends of a tube full of water. They then observed the release of hydrogen near the wire connected to the zinc terminal of the battery and of oxygen next to the other terminal. They also did not fail to notice that the water in the region where hydrogen was liberated became alkaline and that where oxygen was released became acid.

Carlisle and Nicholson waited for the reading of Volta's communication before publishing their results, even though references had already been made to them by some natural philosophers in the press and at conferences. The communication was read before the Royal Society on 26th June and published the following autumn.⁷ Then, in July, Nicholson published the work that he had done with Carlisle in his own journal.⁸ In this, the two scientists noted that the electric current was originated from the chemical action occurring between the metal and the liquid and not from the contact between the metals, as

suggested by Volta, and that the electrical current decomposed water to give oxygen and hydrogen. This was, effectively, the first work in which the two electrical phenomena are stated as proved.

Various researchers tried to interpret the decomposition of water by the electric current, but although a considerable number of theories was presented between 1800 and 1801, none was convincing. With the knowledge available at the time concerning solutions it would not have been possible to find an explanation for the electrochemical processes.⁹

The observation that hydrogen and oxygen are evolved at different sites, separated by the 5-6 cm distance between the two wires carrying the electric current gave Davy¹⁰ the idea that one could obtain the components of chemical substances by electrolysis.



Through a series of ingenious experiments, this scientist was able to obtain oxygen and hydrogen in two separate jars which were connected by a conducting medium such as a piece of a moistened string. Surprised at not being able to obtain the constituents of potash by electrolysis of an aqueous solution of that compound, he applied a current to fused potash and then obtained a globule of potassium at the cathode, metal unknown at the time. The method was subsequently applied to obtain sodium and, later to other metals.

The behaviour exhibited by the compounds relative to electricity led Davy to formulate a theory of chemical affinity. According to him, when two substances were placed in contact with one another electrical charges of opposite signs developed, with bonding resulting from electrostatic interaction. The two parts could be separated by the action of the electric current, with each fragment going to the terminal with the charge of the opposite sign.

Berzelius¹¹ was also interested in electrochemistry. His work on the action of electric current on some diseases, which he presented when he got his degree in medicine, aroused little interest. But in the next year (1803), in collaboration with Hisinger, a rich Swedish mine owner who had been Berzelius' patron at the start of his career, he published work on the decomposition of certain substances by electric current where migration of metals to the negative pole and of non-metals to the positive pole occurred.¹²

However, Berzelius' fame in electrochemistry is associated with the chemical theory of the composition of matter (dualistic theory)



which he proposed in 1811 and formulated more thoroughly eight years later. According to this theory some atoms were positively charged and others negatively. When they combined there was a certain neutralisation of charge, with an excess of either positive or negative electricity occurring in the compound, depending on the nature of the atoms involved. The acids, which contain non-metallic radicals and oxygen, showed an excess of positive electricity; the bases, composed of metals and

oxygen, were excessively negatively charged; salts composed of one acid and one base radical could be decomposed by the passage of an electric current, giving two parts with opposite charges. In Berzelius' time oxygen was thought to take part in everything relating to chemical composition.

The fundamentals of the dualist electrochemical theory were also expressed by Davy, and this gave rise to controversy, still continuing today, as to which of the investigators can really claim priority. This seems to rest with Berzelius, however, possibly because he formulated his theory more explicitly and completely.

The dualist electrochemical theory was accepted, unquestioned, for more than twenty years, and it remained for a much longer period

in some branches of chemistry. The work of Faraday, Daniell and other authors, mentioned later on, as well as those of organic chemists, came to call the theory into question.¹³ However, Ostwald, in his book *Die wissenschaftlichen Grundlagen der analytischen Chemie*, published in 1894, turned against the fact that authors were still, at that time, writing the formula of potassium sulphate as K_2O and SO_3 .¹⁴

Meanwhile there was another problem which was beginning to claim researchers' attention, namely, that of the mechanism whereby liquids conducted electricity. One theory that was accepted by the scientific world for about twenty-five years owed its existence to Grotthus¹⁵ (1805). Electrical conduction through water was explained thus, by this theory: A molecule of water (OH, at the time) was made polar by the action of the electric current, leaving the hydrogen atom positive ly charged and the oxygen negatively charged. The molecules were oriented, then, in accordance with the charge sign of the terminals,



Theodor v. Grotthufs

the hydrogen atom turning to that which had the negative charge and the oxygen atom turning to the other. When the charge at the terminals was high enough it neutra lised the charge in the nearby hydrogen and oxygen molecules, the resulting neutral substances being liberated as gases. The oxygen and hydrogen atoms remaining in the liquid, combined with hydrogen and oxygen of the neighbouring water molecules and, a successive series of decompositions and recombinations

occurring throughout the whole liquid and the initial situation was restored.¹⁶

A new landmark in the history of electrochemistry was established in 1833 with the proposition of Faraday's Law^{17,18} From a practical point of view these laws made it possible to measure the amount of electricity supplied to an electrochemical system. In the theoretical field they contained the essential concept that constituents of matter, that were separated by the action of electrical current, had a fixed



M. FARADAY

amount of charge, and that it was these particles, called ions, that were responsible for transporting elec tricity in solutions. The idea that ions existed in solutions was first suggested by Faraday, although this worker was concerned neither with their origin nor with their number. Besides the designation "ion", several other electrochemical terms, which are still used today, owe their origin to Faraday, e.g. cation, anion, cathode, anode, electrolysis an electrolyte.¹⁹

Faraday's Laws broke through the restraints of the dualistic theory once according to this the amount of current needed to decompose a particular substance depended on its affinity; the greater this was, the greater the amount of current needed for decomposition. This fact gave rise to lively discussion between Faraday and Berzelius.

In the 1840s electrochemistry was enriched by some techniques which contributed significantly to its development by permitting more quantitative results to be obtained.

In 1836 the english chemist, Daniell,²⁰ built a two-liquid battery which bears his name. In contrast to Volta's battery, this one comprised a reversible electrochemical cell. It was the first source of constant potential which allowed accurate results to be obtained. Poggendorf²¹ (1841) published a diagram of an electric circuit for measuring electromotive forces by the compensation method and, two years later, Wheatstone²² published another for measuring electric conductivity.

The experimental data which were being obtained continued, for several years, to cast double on the accepted notions about conduction of current by solutions and on the pivotal question of their struc tural composition.

Daniell did some experiments on electrolysis in which a known amount of current was supplied simultaneously to a dilute solution of sulphuric acid and a solution of sodium sulphate.²³ He noted that

hydrogen and oxygen were released in equal quantities in the two jars containing the solutions, but in that which contained the salt, acid was formed on the anode and base on the cathode in quantities equivalent to those of the released hydrogen and oxygen.



W. Daniell

These results could not be explained by Berzelius' theory, according to which from the observed products of the decomposition, if hydrogen and oxygen from the water and acid and base from the salt, the second jar would require twice as much electricity as the first one. Daniell suggested that the cation Na^+ was discharged from the cathode and the anion SO_4^{2-} from the anode. These discharged species, on combining with the water, led to hydrogen and oxygen, respectively, being formed.

Although this explanation was incorrect one very important conclusion was drawn by Daniell that the charged species which comprised the salt were Na^+ and SO_4^{2-} .

In 1853 Hittorf²⁴ showed that the variation in the ion concentration in the proximity of the electrodes was dependent on the mobility of the ions. During the next six years he determined the transference number (a concept introduced by him) of several species in solutions²⁵ These results did not arouse much interest at the time, but they were eventually important in that they served as a base for the theoretical development which came after him and it is, for this reason that he has remained as one of the classic references in the history of electrolytic solutions.

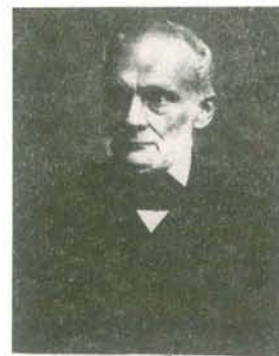


H. Hittorf

Kohlrausch²⁶ investigated the elec

trical conductivity of solutions and introduced some innovations in the techniques of determination, such as the use of an alternating current to prevent polarisation and the telephone instead of the galvanometer.²⁷

From 1876 to 1879 he produced a useful set of results from which



A. Clausius

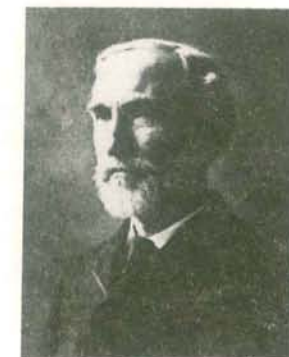
he drew some important conclusions, namely, that the velocity of an ion is not dependent on other ions with which it was forming molecules, and that electrolytes conduct the electric current even when the applied current has low-value potentials.²⁸

Grotthus' theory, which held sway for twenty years as the explanation of electric current conduction in solutions, was cited by Clausius²⁹ in 1857. The arguments used by this famous mathematician/physicist were based on experimental evidence of conduction

occurring even when the potential of the applied current was low. This fact indicated the existence of free ions in the solution, since if these were the result of the action of the electric current on the molecules, then conduction would only occur at potentials above a given value.³⁰

According to Clausius the ions would come from molecular vibrations which would have an energy greater than that required for molecular decomposition. The charged particles thus formed, even if small in number, would ensure transport of the current.

In the period from 1890s into the first decades of the 20th century, electrochemistry was dominated by thermodynamics. After the work by Gibbs³¹ and Helmholtz³² the application



J. William Gibbs

of thermodynamic principles to chemical phenomena became the methodology followed in studying them. The theories developed by these two scientists,

especially by Gibbs, constituted mathematical generalisations of fundamental concepts which were shown as virtually inexhaustible sources of supply.

Gibbs' work, published in three proceedings of the Trans. of Academy of Connecticut between 1876-1878, had no immediate impact on chemistry, partly because the journal in which it was published was not very known, and, mostly on account of its mathematical nature, it did not become easily accessible. It was divulged by means of translation, application and development of theories on one or another of them by noted scientists.



J. Willard Gibbs

Ostwald³³ is one figure who can be highlighted in this period. He had distinguished himself as a research worker, author and editor. In 1887 he founded

the journal *Zeitschrift für Physikalische Chemie* dedicated to physical chemistry, a new discipline that came into being with thermodynamics. Works of enduring fame in the history of electrochemistry, and chemistry itself, were published in it.

In the first volume of this journal, Van't Hoff³⁴ published an article on the theory of osmotic pressure which became very important with the development of the chemistry of solutions.³⁵ In this article the author demonstrated that dilute solutions exhibited a behaviour similar to that of the gases which obeyed the Boyle-Mariotte and Gay-Lussac Laws.



W. Ostwald

But almost at once Van't Hoff discovered that electrolytic solutions behaved in an anomalous way, making it necessary to introduce a coefficient i (always greater than one) in the equation of gases when applied to these solutions.

Another famous article was published in the first volume of *Z. Phys.*

Chem. by Svante Arrhenius.³⁶ In it he expounded his hypothesis of electrolytic dissociation. This was not his first publication on the theory, since it had been presented in his doctoral thesis from Upsala



University. Arrhenius extracted two papers, published in the *Bihang* of the Swedish Academy of Science in 1884, from his thesis.³⁷

In view of the difficulty he had encountered in getting his ideas accepted by the University's professors, Arrhenius had recourse to international help, sending reprints of his publications to famous European scientists. The most effective reply came from Ostwald, whose recognition of the new theory's worth was an important factor in his argument and dissemination,

battle to which Van't Hoff associated himself. It was just at that moment when the article was published in *Z. Phys. Chem.*, setting down the theory in a more complete form which supporting evidence from chemical, electrical and thermodynamic data.³⁷ The new theory gave a satisfactory explanation for the reactions of various compounds in solution, the results obtained by Kohlrausch and by Arrhenius himself for electrical conduction, the need to introduce the coefficient i (as shown by Van't Hoff) in the osmotic pressure equation. The results which had, meanwhile, been obtained, as Ostwald's dilution law formulated in the following year, served as a test for it.³⁸



S. ARRHENIUS

Arrhenius' theory was an historic landmark, not only for making fundamental aspects of the structure of electrolytic solutions, but also as a firm starting point for studying the properties of these solutions.

As the existing entities in solutions being charged particles,

the electrolytic dissociation theory opened two areas for scientific research; the interaction of the ions with one another, and the interaction between them and the solvent molecules. These domains,



P. DEBYE

however, did not emerge by a natural process of extension of the field of research but rather as attempts to explain anomalous behaviour shown by the strong electrolytes. It was proved early on that for these solutions the increase in concentration affected their thermodynamic properties (osmotic pressure and cryoscopic depression) and their electrical conductivity. The values obtained for the degree of electrolytic dissociation, calculated by the different properties,

decreased with an increase in concentration.

Arrhenius attributed the observed effects to the incomplete dissociation of the electrolyte at finite concentrations. For other workers these would be the result of the formation by the ions of other chemical species in solution, e.g. complexes.

Alongside these attempted explanations involving a chemical basis, others were proposed which assumed that dissociation is complete, but that the deviation from the behaviour of infinitely dilute solutions was produced by ionic interactions.

The first investigator to call attention to the possible effects of particularly intense electric fields of ions was Van Laar.³⁹ Some years later, Sutherland tried to interpret the decreases in conductivity by ionic interactions.⁴⁰ Reference should also be made to the studies of Bjerrum, who confirmed the influence of intermolecular forces by means of the absorption spectra of chromium salts.⁴¹ However, the first quantitative treatment of these interactions is due to Milner, who, started producing a physical model which was identical to that accepted by Debye and Huckel a decade later.⁴² Milner's theory was more complicated mathematically, however, and so did not achieve much success. In 1923, Debye⁴³ and Huckel⁴⁴ like Milner, acknowledged that the ionic distribution could be given by a Boltzmann equation, but whereas the latter used a complicated probabilistic treatment to determine the potential

energy, Debye and Huckel used the Poisson equation to relate the charge density to the potential.⁴⁵ Following from the above two equations, they succeeded in deriving an expression for the coefficient of deviation of the behaviour of electrolytes relative to the ideal state at infinite dilution, although it was only applicable to dilute solutions. It is worth noting that in such a basic treatment Debye and Huckel had the merit of providing a simple theory on ionic interactions which was able to explain any of the anomalies attributed to electrolytes.

The solvation sparked the attention of chemists from the end of the previous century. However, it was only with Born, in 1920, that it was treated in quantitative terms.⁴⁶ From then it became an area of great scientific activity, particularly after the 1960s.

In spite of the importance that these two scientific areas have in the understanding of electrochemical processes, the number of significant works carried out in them recently is so great that it is totally impossible to give an account, in a presentation such this, of each one's evolution. At this point we will end the description of the history on ionic solutions.

Most electrochemical systems are heterogeneous, consisting of an electrode in contact with a solution. The electrode acquires electrical charge, resulting from a chemical reaction between itself and the solution (as with galvanic cells), or applied from an external source (as with electrolytic cell).



W. Nernst

The first studies on the theory of the electrode potential were carried out by Nernst,⁴⁷ who was one of the best known figures of physical chemistry at the turn of the century. He was the author of a large number of experimental, and above all, theoretical work.

His book *Theoretische Chemie*, published in 1893, was considered a standard work for some thirty years. In 1889, Nernst derived the well known equation of the electrode potential $E = \frac{RT}{n} \ln \frac{P}{p}$, where P is the "solution

pressure" of the metal, p is the "osmotic pressure", and E is the potential difference metal/electrolyte.⁴⁸ This equation was later given in terms of concentration, and subsequently entered the history of electrochemistry as the Nernst equation. As a detail we should say that the concept of E introduced by Nernst and criterion of the sign, which differed from that used by Gibbs ten years earlier, has given rise to a conflict of signs that has continued to the present day.^{a)} As a result of its thermodynamic base, the Nernst equation is only applicable to reversible electrodes under conditions of null current.

Electrode processes are associated with a reaction between electrode and solution that occurs in a given direction at a finite rate. They are, consequently, kinetic processes the understanding of which requires a detailed knowledge of the interface between the electrode and the solution.

The first model of the interface came in the works of Helmholtz. In 1853 he described the distribution of charges formed by two metals in contact as two charge layers that are separated by a distance of atomic dimensions.⁴⁹ He called this array of charges a "double layer". Some years later (1879) he identified the interface of a metal and an ionic solution with that described for two metals, where the electrical charge of the electrode is neutralised by the charge of the ions of the solution distributed in a plane parallel to its surface.⁵⁰ The electrode surface and the plane defined by the ions was similar to an electrical condenser.

As a result of studies concerning the mercury/aqueous solution interface for electrolytes, Gouy (1910) and Chapman (1913) independently proposed a theory for the ionic distribution at the interface.^{51, 52} This involved a diffuse charge distribution, resulting from the appli-

a) For Nernst E is the potential difference metal/electrolyte being then a bivalent quantity as far as it depends on the direction assigned to the electrode process. Gibbs proposed the "electrical potential" of an electrode defined as a measurable electrical potential difference between "two pieces of the same kind of metal connected with the electrode under consideration and with the reference electrode". E is therefore an univariant quantity. Nernst considered E being positive as the solution becomes positive and the metal negatively charged, what is the opposite to Gibbs' convention.

cation of Boltzmann's law and Poisson's equation. It is to be referred that a similar treatment was adopted by Debye and Huckel a decade later for electrolyte solutions.

In 1924, Stern⁵³ proposed a theory which encompassed the previous two models. The interface was, as such, divided into two regions: the layer closest to the surface having immobilised ions, with the rest involving diffusely distributed ions.⁵⁴

Results obtained for electrocapillary curves of mercury with different solutions of different salts led Grahame to propose a more complete formulation.⁵⁵ In this model a distinction is made between the two distances of closest approach of metal ions to the electrode according to whether the interaction is exclusively electrostatic, or whether other contributions are considered (specific adsorption). Still, the layer outside this region is of diffuse type.

Both the quantitative models of Gouy and Grahame were established on the basis of results obtained with the mercury electrode, for which the charge can be considered to be uniformly distributed over the whole surface. This approximation is, however, not satisfactory for other surfaces, for which models have been sought based on the discreteness of the surface charges specifically to each of the systems.

Electrochemical kinetics is an area developed more recently, although some studies in this direction had been carried out at the turn of the century. In 1903, Tafel, in a study concerning the discharge of the hydrogen ion, obtained an equation relating the current intensity with the overvoltage.⁵⁶ However, the mechanism presented in this study was still largely influenced by thermodynamics. The hydrogen ion would reach the electrode surface at a potential corresponding to equilibrium. The slow part of the process was the combination of hydrogen atoms formed on the surface of the electrode to produce molecules of gas. As such, to obtain a finite intensity of the current it is necessary to change the potential in the cathode direction, which would increase the concentration of ions adjacent to the electrode and the hydrogen pressure on the surface, in order that the reaction would occur with a finite rate. Already, before this, Caspari had recognised that to have liberation of hydrogen or oxygen it was necessary to apply different potentials that depended on the nature of the metals used, both for the cathode and anode.⁵⁷ The difference between the potential needed for

liberation of gas and the theoretical value corresponding to the reversible process was called "uberspannung", a term which was translated as overpotential or overvoltage. Tafel derived an equation which related the overpotential with the current intensity, which has become known by his name.

The involvement of the structure of the electrical double layer in the kinetic processes only came to be used from the 1930s. Erdey-Gruz and Volmer were the first to obtain an equation that related the current density with the overpotential.^{58,59} This quantity was, however, defined in a somewhat imperfect form. For them, the overpotential was a potential difference corresponding to the electrostatic work to be supplied to the ion, such that it could pass the energy barrier at the interface from a position on the solution side to a position on the electrode surface.

Contemporary with the works of these authors were those carried out by the Russian School, directed by Frumkin.⁶⁰ These workers interpreted the electrode processes in terms of parameters characteristic of the electrical double layer.

A treatment of electrode kinetics in quantum mechanical terms was made by Gurney in 1932.⁶¹ For him, the overpotential corresponded to a displacement of the Fermi levels that allowed the electron of the metal to have energies overlapping with vacant acceptor levels (given by a Boltzmann equation) in molecules adjacent to the electrode.

This theory did not kindle interest, and the treatment of the kinetics on the basis of quantum mechanics was only returned to in the 1960s.

REFERENCES

In the preparation of this work some books and papers on electrochemistry, the history of science and scientists' biographies have been consulted. Among these publications we should refer to,

W. Ostwald, *Electrochemie, ihre Geschichte und Lehre*, Veit und Co, Leipzig, 1906; Max Le Blanc, *The elements of Electrochemistry*, translated from German by W.R. Whitney, McMillan and Co, London, 1896; F. Szabadváry, *History of Analytical Chemistry*, translated from Hungarian by Gyula Svehla, Pergamon Press, London, 1966; H. Falkenhagen, *Electrolytes*, translated from German by G. Mano, Librairie Félix Alcan, Paris, 1934.

We think it to be of some help together with the references to include some biographic notes on the leading scientists to whom we are indebted for their contribution to the development of electrochemistry. Unfortunately the time available did not allow us to do this for all those included in the text.

1. GALVANI, LUIGI (1737-1798). Galvani was appointed professor of anatomy at the University of Bologna and moved later to professor of obstetrics at the same university. He dedicated himself to research on the influence of electricity on animal tissues. During his experiments he noticed that a freshly prepared frog's leg twitched when a nearby frictional electric machine was running and the crural nerve was touched by a scalpel. This unexpected observation led to research for a few years on this subject and the attempt to find an explanation for the phenomenon led to the birth of electrochemistry. Galvani had a great moral character and defended his ideas with great courage. When Napoleon occupied Italy in 1797 he refused to accept the new regime and was dismissed from his chair. Without any income he lived in extreme poverty and died in the following year.
2. Galvani, L. *De Bononiensi Scientiarum et Artium Instituto atque Academia Commentarii*, Tom VII, 363-415 (1791).
3. VOLTA, ALESSANDRO (1755-1827). Volta was born in Como into an aristocratic family. Well educated by an uncle he devoted himself early on the study of electricity, then an epoch-making subject and corresponded with well-known experimenters. He published his first paper at the age of twentyfour. After being superintendent and later professor of physics of schools in Como four years he was appointed in 1778 professor experimental physics at the University of Pavia. He travelled over all Europe and made friends and acquaintances among the leading people in science of different countries. He invented some physical instruments, the most important being the famous electric pile which played an important role in the development of electrochemistry. He retired in 1819 and lived in his birth place until death. Very few scientists received in life as many homages and honours as Volta. In 1791 he had been made a foreign member of the Royal Society. Napoleon made him Count and he became a senator of the Kingdom of Lombardy.

4. RITTER, JOANN-WILHELM (1776-1810). Ritter was born in Samnitz, Silesia (now in Poland). After working for four years (1791-1795) as a pharmacist's apprentice he went to Jena to study medicine. He taught at the Universities of Jena and Gota and practised medicine in these two places. In 1804 he moved to Munich as a member of the Bavarian Academy of Science. Between 1800 and 1802 he conducted scientific investigation on the chemical effects of electricity and developed a dry battery. In 1804 he established an electrochemical series based on order by which the metals precipitate one another from solutions of their salts. He also discovered the ultraviolet rays by their effect on silver chloride and related the energy of these rays to that of visible spectrum (1801-1803). For his work on electrochemistry Ostwald considered him as the founder of this science.
5. CARLISLE, ANTHONY (1758-1840). Carlisle was the head of the Westminster Hospital in London and physician of the Prince of Wales. He was a member of the Royal Society.
6. NICHOLSON, WILLIAM (1753-1815). Nicholson was an engineer and was at first a clerk with the East India Company and then head master of a school in London. Later he became a private engineer and designer of hydraulic canals. Simultaneously with his professional duties he dedicated himself to chemistry, being the author of the *Dictionary of Chemistry* published in 1795. He was the owner of the *Journal of Natural Philosophy, Chemistry and Arts* known as *Nicholson's Journal* where were published many papers on electrochemistry in the early 1800's.
7. *Phil. Trans.* 90, 403 (1800).
8. Carlisle, A. and Nicholson, W. *Nicholson's J.*, 4, 181 (1800); *Gilb. Ann.*, 6, 340 (1800).
9. *Vide* Sudduth, W.M., *Ambix*, 27, 26 (1980).
10. DAVY, HUMPHRY (1778-1829). Davy was born at Penzance, Cornwall and was the eldest of two brothers and to sisters. His father, a woodcarver, died when Humphry was sixteen. At this age he went to a surgeon-apothecary as apprentice and began to study chemistry. In 1798 he joined the famous Pneumatic Institute in Bristol founded to study the medical effects of gases. He left this Institute three years later for having been appointed assistant lecturer of the Royal Institution. His experimental skill and eloquence led him soon to lecturer and professor of chemistry. In 1806 he obtained potassium, an unknown element, by electrolysis fused potash, and later sodium from fused soda using the same method. These events confirmed his own theory that the chemical combinations were polar in nature. He obtained magnesium, calcium, strontium and barium by distilling their amalgams prepared electrolytically. He proved that chlorine was an element and that muriatic (hydrochloric) acid had no oxygen, thus demonstrating that Lavoisier's concept of acids as an oxide of a non-metal was incorrect. Anaesthetic properties of nitrous oxide (1798), miner's safety lamp (1815), cathodic protection of copper bottomed ships zinc plates (1824) were some Davy's inventions. He travelled through all Europe.
- From 1820 to 1827 he was president of the Royal Society and in 1812 was knighted and created baronet six years later. He resigned from the Royal Institution owing to a ill health in 1827.

11. BERZELIUS, JÖNS JACOB (1779-1848). Berzelius was born at Väversunda in Ostergotland, a province of Sweden, into a family traditionally dedicated to clergy. He had an uneasy childhood and youth as a consequence of his father's death when he was four and of his mothers's a few years later. He received a medical degree in 1802 from the University of Uppsala and three years later he was appointed professor of medicine and pharmacy at Stockholm. Elected to the Swedish Academy of Sciences in 1808 he was appointed secretary eight years later, a paid office which allowed him for the first time to reach a social position corresponding to his scientific authority. The period 1810-30 is sometimes called period of Berzelius owing to the importance of his work and because through his small kitchen laboratory passed leading chemists such as Gmelin, Misterlich, Rose, Wöhler. He began working on electrochemistry in 1802 sponsored by a rich mine owner Wilhelm Hisinger. Using reagents prepared by himself he determined the atomic weight of 45 out of the 48 chemical elements known at the time by gravimetric techniques which represents a giant's task. There come from him the symbols used now for representing the elements. He discovered some elements and isolated some others. He made some contributions to almost all branches of the chemistry of those days. His most important contribution to electrochemistry was the dualistic theory.
12. *Gehlens Journal für Chemie*, 115 (1803).
13. In 1834 the french organic chemist August Laurent (1807-1853) observed that it was possible to obtain trichloroacetic acid by reacting acetic acid with chlorine. He formulated his 'substitution theory' according to which some elements in molecules could be substituted by others without destroying the molecular building. This theory contradicted that of Berzelius as an electropositive element was substituted by an electronegative one.
14. W. Ostwald, *Die Wissenschaftlichen Grundlagen der Analytischen Chemie*, Leipzig, 1894.
15. GROTHUS, THEODOR (1785-1822). Theodor von Grotthus was a landowner in Lithuania dedicated to science as a hobby. He had the title of baron.
16. *Ann. Chim. Phys.*, 58, 54 (1806); 63, 20 (1808).
17. FARADAY, MICHAEL (1791-1867). Son of a poor blacksmith, Faraday was born at Newington Butts, near London. At thirteen he went to London as a bookseller's apprentice. His interest in electricity and chemistry arose early. Through a customer of his shop he obtained tickets to go to the Royal Institution to attend Davy's lectures. He wrote to Davy for a job in the Royal Institution and was employed in 1813 as a humble assistant. He followed Davy in his travelling through Europe having the opportunity to meet important scientists. Between 1821 and 1831 he did three famous experiments on electromagnetism which had a profound influence in physics and the basis of three important industrial devices, the electric motor, the dynamo and the transformer. In 1834 he discovered self-induction simultaneously with Henry in the United States. Faraday did some research on chemistry (study of compounds of carbon and chlorine, liquefaction of chlorine, isolation of benzene, etc). In electrochemistry he established in 1833-1834 the two laws known by

his name. Davy was jealous of his assistant and in 1824 during Faraday's election as fellow of the Royal Society the only vote against came from Davy. However when once someone asked him which was his best discovery - 'Faraday' was the answer.

18. *Phil. Trans.*, 123, 23 (1833); 124, 77 (1834).
19. For introducing the new terms Faraday had the collaboration of Dr. Whewell, professor at the University of Cambridge, philosopher and mathematician who was a great authority on philology.
20. DANIELL, JOHN FREDERIC (1790-1845). Daniell was born in London and after receiving private education he began to work in a relative's sugar refining factory. In 1831 he was appointed professor of chemistry at the King's College in London, position he held until his death (he died at a meeting of the Royal Society). His main contributions to electrochemistry were the cell called after him that was invented in 1836 and his research carried out between 1839-1844 on the identification of the species separated by electric current as passing through solutions. Work in other fields carried out by Daniell includes the improving processes of sugar manufacturing, invention of a new type of dew-point hygrometer (1820) and a pyrometer (1830). He dedicated also to studies on meteorology.
21. POGGENDORF, JOHANN CHRISTIAN (1769-1877). Poggendorf was a pharmacist and professor at the University of Berlin. He was the editor of *Annalen für Physik*.
22. WHEATSTONE, CHARLES (1802-1875). He was firstly a musical instrument maker in London and at the same time worked in physics. In 1833 he presented to the Royal Society an important paper on acoustics and in the following year he became professor of physics at King's College in London. He invented components of telegraph systems and scientific instruments and distinguished himself in research in electrical science. In 1868 he was knighted. After retiring he lived from the royalties of his many patents.
23. *Phil. Trans.*, 129, 97 (1839); 130, 209 (1840); 134, 1 (1844).
24. HITTORF, JOHANN WILHELM (1824-1914). Hittorf was a professor of physics and chemistry at high school in Munster. His work was mainly on transference numbers.
25. *Ann. Physik.*, 89, 177 (1853); 103, 1 (1858); 106, 337, 513 (1859).
26. KOHLRAUSCH, FREDERIC (1840-1910). F. Kohlrausch was professor of physics at the Technical University of Zurich and after at the universities of Wurzburg, Strasbourg and Berlin.
27. *Gott. Nach.*, 415 (1868). *Ann. Physik*, 138, 280, 370 (1869).
28. *Ann. Physik.*, II, 653 (1880); 154, 215 (1875).
29. CLAUSIUS, RUDOLF JULIUS EMANUEL (1823-1888). Rudolf Clausius was a German physicist and mathematician, being professor at the University of Wurzburg and later at Bonn. He was a brilliant scientist and was one of the founders of thermodynamics. His thesis published in 1850 *Über die bewegende Kraft der Wärme und die Gesetze, welche sich daraus für die Wärmelehre selbst ableiten lassen* contains the basis of the second Law of thermodynamics. According to Willard Gibbs "This thesis marks an epoch in the history of physics and the beginning of thermodynamics as a science". Four years later he introduced the concept of

entropy leading to a new formulation of the Second Law and in 1865 he introduced the term 'entropy'. This work contains the famous sentences: *Die Energie der Welt ist constant. Die Entropie der Welt Strebt einem Maximum Zu*. He made important contributions to the theory of gases and of the electric conduction by liquids. He was made member of many academies.

30. *Ann. Physik*, 101, 338 (1857).
31. GIBBS, JOSIAH WILLARD (1839-1857). Willard Gibbs was born at New-Haven in Connecticut and graduate at Yale University where he was a professor for thirty four years. After obtaining the Ph.D. degree he studied in Paris, Berlin and Heidelberg. In 1869 he was invited to become professor of mathematical physics in Yale, chair occupied by him until his death. He was an outstanding scientist and his work on thermodynamics gave rise to chemical thermodynamics and to the birth of physical chemistry. His work was written in mathematical terms and thus only understood by the chemists after being publicised by famous European scientists such as: van der Waals, Ostwald, Van't Hoff, Le Chatelier. Among his writings, all very important, ones which should be placed at the top are three reports published in the Transactions of the Connecticut Academy of Sciences *A method of geometrical representation of the thermodynamic properties of substances by means of surfaces* (Dec. 1873); *On the equilibrium of heterogeneous substances, Part I* (June 1876); *Ibid Part II* (July 1878) and *Elementary principles in statistical mechanics developed with special reference to the rational foundation of thermodynamics* (1902). He was a modest man with a kind personality and his life was a model of dignity.
32. HELMHOLTZ, HERMANN LUDWIG FERDINAND VON (1821-1894). Helmholtz was born in Postdam and studied medicine in Berlin. He was professor of physiology at the universities of Königsberg, Bonn and Heidelberg. In 1847 he presented to the Physical Society of Berlin the paper *On The Conservation of Force* where he clarified the conservation of energy principle. He wrote on physiological optics and acoustics. In 1870 Helmholtz became professor of physics in the University of Berlin and in 1888 he concurrently served as the director of the German Bureau of Standards. He made important contributions to thermodynamics and to electrochemistry. In 1882/83 independently of Gibbs, he introduced the free energy function and established its relations to the chemical affinity, the heat of a reaction and the electromotive force of a galvanic cell. The first proposal of a model for the electrical double layer came from him.
33. OSTWALD, WILHELM (1853-1932). Ostwald was born in Riga into a wealthy family. He graduated from the University of Dorpat where he remained as a lecturer after completing his studies. From 1882 he occupied the chair of chemistry at the Technical University of Riga for five years. After this period he went to the University of Leipzig where he founded an Institute of Physical Chemistry which became famous all over the world. He introduced several important concepts in chemistry and wrote several books. His book on analytical chemistry is a pioneering work in putting this scientific branch of chemistry on a theoretical basis. He was an untiring worker as researcher, editor and organizer. In 1887 he founded a journal dedicated to physical chemistry *Zeitschrift für Physikalische Chemie Stoichiometrie und Verwandtschaftslehre* that he edited jointly with Van't Hoff.

This journal played an important part in the development of physical chemistry. Between 1891 and 1901 he produced important work on catalysis, linking it to chemical kinetics. He remained all his life an opponent (one of the last) to the atomic theory and believed that thermodynamics could be used to explain all chemical phenomena. He retired in 1906 and two years later he was awarded the Nobel Prize for Chemistry for his work on catalysis and chemical equilibrium.

34. VAN'T HOFF, JACOBUS HENDRICUS (1852-1911). Van't Hoff after completing his studies began his career as professor at the Veterinary School of Utrecht. He moved in 1878 to the University of Amsterdam where he was a professor until 1896. He was then invited by the Prussian Academy of Sciences to do research and moved to Berlin. Van't Hoff proposed fundamental theories for new developing areas in organic and physical chemistry. Independently Van't Hoff and J.A. Le Bell proposed the theory of the asymmetric carbon which led to stereochemistry. His work on chemical kinetics 'Études de Dynamique Chimique' published in 1884 was fundamental for the development of chemical kinetics. His theory on osmotic pressure played an important role in the establishment of the modern theories of electrolyte solutions. Van't Hoff was one of the scientists who contributed to the birth of physical chemistry as an independent branch of chemistry. He was the first Nobel Laureate in chemistry (1901), reward for his work on 'chemical dynamics' and 'the osmotic pressure of solutions'.
35. *Z. phys. Chemie.*, 1, 481 (1887).
36. ARRHENIUS, SVANTE AUGUST (1859-1927). Arrhenius was born in Wijk, a place near Uppsala, son of an estate manager. His family name comes from Arena a village from where his ancestors came. In the year following his birth the family moved to Uppsala where he was educated. He went to Stockholm to study for his doctorate as Professor Cleve at Uppsala with whom he wanted to work, was not interested in the theoretical side of chemistry. In 1883 he submitted the thesis to the University of Uppsala and got a modest fourth class classification. Independently his theory he received considerable help from Ostwald and Van't Hoff, specially from the first. The theory finally prevailed after a battle of almost six years. In 1885 he initiated a five-year scholarship from the Swedish Academy of Sciences giving him the chance to work with Van't Hoff, Ostwald, Boltzman and Kohlrausch. In 1891 he was appointed lecturer in the Technical University of Stockholm and professor four years later. In 1905 he became director of the Nobel Institute for Physical Chemistry. His later scientific work was on the theory of reaction rates. He received numerous medals and awards. In 1903 it was awarded the Nobel Prize in chemistry for his theory of electrolytic dissociation.
- 36a. *Bihang der Stockholmer Akad.*, 8, 13 and 14 (1883).
37. *Z. Phys. Chem.*, 1, 631 (1887).
38. *Z. Phys. Chem.*, 2, 36, 270 (1888); 3, 170, 241, 369 (1889).
39. Van Laar, J.J., *Z. Phys. Chem.*, 15, 457 (1894); 17, 245 (1895); *ibid.*, 18, 274 (1895); *ibid.*, 18, 318 (1896).

40. Sutherland, W., *Phil. Mag.*, 3, 161 (1902); *ibid.*, 9, 781 (1905); *ibid.*, 12, 1 (1906); *ibid.*, 14, 1 (1907); *ibid.*, 16, 497 (1908).
41. Bjerrum, N., *Proc. 7th Internat. Congress of Appl. Chem.*, London, 1909 Sect. X; *Z. Anorg. Chem.*, 63, 146 (1909).
42. Miller, S.R., *Phil. Mag.*, 23, 551 (1912); *ibid.*, 25, 742 (1913); *ibid.*, 35, 214, 352 (1918); *Trans. Faraday Soc.*, 15, 148 (1919).
43. DEBYE, PETER JOSEPH WILHELM (1884-1966). Debye was born in the Netherlands and received his doctorate at the University of Munich in 1908. Before the second world war he taught at various European universities and was director of the Max Planck Institute of Berlin. In 1940 he went to United States and was appointed professor at Cornell University. While in Europe he made important contributions to the study of vibrations in molecules by many methods and problems of crystal structures and dipole moments. On the electrochemistry side he worked out a theory of ionic interaction. He received the Nobel Prize for Chemistry in 1936 for his research on molecular structure. In the United States his investigations were directed towards the structure and size of high molecular weight polymers.
44. HÜCKEL, ERICH ARMAND ARTHUR JOSEPH. Hückel was born in Berlin-Charlottenberg in 1896 and three years later his family moved to Göttingen. He studied physics in the local university and in 1921 he obtained the doctorate, presenting a thesis on the diffraction of x-rays by liquids prepared under the guidance of P. Debye. After being in Göttingen for two years he went to the Zurich Technische Hochschule to join Debye. In 1930 he went to the Stuttgart Technische Hochschule where he was for seven years, then becoming professor of theoretical physics at the University of Marburg. With Debye he developed a theory on the ionic interaction of electrolyte solutions. In 1930 he began research on the theory of aromaticity.
45. Debye, P. and Hückel, E., *Physikal. Z.*, 24, 185, 334 (1923); *ibid.*, 25, 97 (1924); *Rec. Trav. Chim.*, 42, 597 (1913).
46. Born, *Z. Elektrochem.*, 26, 401 (1920).
47. NERNST, WALTER HERMANN (1864-1941). Walter Nernst was born in Thom and studied at Zurich, Graz and Würzburg. After receiving his doctorate at Würzburg he became assistant to Ostwald in Leipzig. He went to Göttingen in 1891 and three years later he became professor of the first department entirely devoted to physical chemistry. In 1904 he was invited by the University of Berlin to occupy the vacancy left by Landolt. In 1922 he became the director of the Physikalische Technische Reichsanstalt, a position he held until retired in 1933. He had a mathematical brain and expressed easily the laws of physical chemistry in mathematical terms. In Ostwald's Institute he developed his theory of the osmotic pressure of galvanic cells (1889). In 1906 he enunciated the Third Principle of Thermodynamics, the heat theorem, for which he received the Nobel Prize in 1920. Later he worked on photochemical chain reactions and astrophysics. Besides his theoretical work he also did very good experimental work in different areas.

48. Nernst, W., *Z. Phys. Chem.*, **4**, 129 (1889).
49. Helmholtz, H., *Pogg. Ann.*, **89**, 211 (1853).
50. Helmholtz, H., *Ann. d. Physik u. Chemie (Wiedemann's Ann.) N.F.*, **7**, 337 (1879).
51. Gouy, G., *J. Phys. Radium*, **9**, 459 (1910).
52. Chapman, D.L., *Phil. Mag.*, **25**, 457 (1913).
53. STERN, OTTO. Stern was born at Sohrau, Upper Silesia, Germany, in 1888. As a child he moved to Breslau where he studied for his graduate and post-graduate degrees. After his doctorate he joined Einstein at the University of Praga and later followed him to the University of Zurich where he became privadocent of physical chemistry at the Eidgenossische Hochschule for one year. He taught in several european universities. he was privadocent of theoretical physics at Franckfurt-am-Main (1914-21), Associate Professor of theoretical physics at Rostock (1921-22), Professor of physical chemistry at the University of Hamburg (1923-33). On the rise of Nazism he went to the United States and was appointed professor at the Carnegie Institute of Thecnology in Pittsburg. Until 1919 he worked in the field of theoretical physics and after mainly in experimental physics. He received the 1943 Nobel Prize in Physics for his discovery and measurement of magnetic moment of the proton. His theory on the electrical double layer was published when he was at Hamburg.
54. Stern, O., *Z. Elektrochem.*, **30**, 508 (1924).
55. Grahame, D.C., *Chem. Rev.*, **41**, 441 (1947); *J. Am. Chem. Soc.*, **76**, 4819 (1954); *ibid*, **79**, 2093 (1957).
56. Tafel, J., *Z. Phys. Chem.*, **50**, 641 (1905).
57. Caspari, W.A., *Z. Phys. Chem.*, **30**, 89 (1899).
58. Erdey-Gruz, J. and Volmer, M., *Z. Phys. Chem.*, **150 A**, 203 (1930)
59. Erdey-Gruz, J. e al., *Z. Phys. Chem.*, **162 A**, 53 (1932).
60. Frumkin, A.N. et al., *Z. Phys. Chem.*, **164 A**, 121 (1933); *Acta Physico-Chim. URSS.*, **7**, 475 (1937); *ibid*, **12**, 21 (1939); *ibid*, **12**, 481 (1940).
61. Gurney, R.W., *Proc. Royal Soc.*, **134 A**, 137 (1931).

THE GROWTH OF ELECTROCHEMISTRY IN THE UNIVERSITY OF COIMBRA FROM THE BEGINNING TO THE PRESENT^{a)}

J. SIMÕES REDINHA

Departamento de Química, Universidade de Coimbra, 3000 Coimbra

The study of Chemistry at the University of Coimbra began with the 1772 reform, normally known as the Pombaline reform (after the Marquis of Pombal, King Joseph I's Prime Minister). This was a profound reform of the University and among its great innovations the study of the experimental sciences is one of them. A new Faculty was then created - the Faculty of Philosophy - dedicated to these sciences. The fourth year of the philosophical course, the last one, was occupied with the chair of chemistry "Theoretical and Practical Chemistry".

The same reform also stipulated the construction of the "Laboratório Químico" intended for the practice of chemistry. The building was in fact concluded in three years which is remarkable for the time. For two centuries it served as the centre of chemistry studies of the University of Coimbra.

The progresses registered in chemistry until the end of the eighteenth century may be considered satisfactory for the starting of a new science in a small country without much scientific tradition and did not contrast much with the development of this science in the rest of Europe, busy with the conflict between Lavoisier's chemistry and the phlogiston theory.

a) Based on the invited lecture delivered at the Celebratory Session of the 5th Anniversary of the Portuguese Electrochemical Society, Lisbon, 1989.