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CHEMICAL ELECTRICITY

Abstract: In 1800 Alessandro Volta published the results of several years' work on the phenomenon of electric shocks which he experienced from physical contact with the terminals of his newly developed battery. His work was prompted by Luigi Galvani's explanation of involuntary muscle spasms in frog's legs, which he induced and attributed to animal electricity. Volta's paper opened the floodgates for research in the new field of electrochemistry which has resulted in today's worldwide electric battery industry. This essay explains the sequence of natural events and their explanations which led to the publication of Volta's paper, and gives an overview of the scientific research resulting from Volta's work. This research includes attempts to improve batteries, and the development of ideas which led to a better understanding of matter and the way it interacts with energy. Practical details for the teaching of several important chemical concepts are listed in the appendix. The experiments are related to a reaction which has been known for many centuries - that between iron and copper sulphate solution.

Keywords: Galvani, Volta, natural philosopher, history of electricity, electrochemistry, electric cell, battery

Introduction

On 26 June 1800 the Italian Professor of Natural Philosophy Alessandro Volta [1745-1827] published a letter in the Philosophical Transactions of the Royal Society. The letter, written in French, was addressed to the Right Honourable Joseph Banks [1743-1820], who was president of the Society. Its title was "On the Electricity excited by the mere Contact of conducting Substances of different kinds" [1].

Volta described a kind of electricity which was generated from two metals which were in contact with a saline solution. This electricity was a form of energy which was able to produce dramatic effects on the human body. In his letter, Volta mentioned the frequently painful consequences of self-inflicted electric shocks. They included: tingling, jolts, spasms, convulsions, and violent flashes and sounds, seemingly in his head. The effects were produced by connecting various parts of his body - tongue, cheeks, forehead, lips, nose, eyes, eyelids, mouth, fingers and hand - to the terminals of his battery.

He constructed batteries which consisted of piles of discs of two different metals, arranged alternately and interspersed with card/leather which was impregnated with saline solutions. The batteries consisted of 30, 40 or even 60 cells. He tried varying combinations of pairs of different metals and found that zinc and silver gave the most dramatic effect.

On account of the dramatic effects on his own body which Volta described in his letter, and the way in which the effects were produced, its publication caused a sensation and opened the way for an avalanche of research by scientists throughout Europe.

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Historical background

The interpretation of natural phenomena has gradually evolved through the ages: magic and superstition, philosophy, science. Since the third century BC, explanations of volcanic eruptions, changing weather patterns, chickens hatching from eggs, acorns growing into oak trees, breathing, burning, had been provided by philosophers, of whom the Greek Aristotle [384-322BC] had been a key figure. As a result of his observations over several decades, his explanations were logically and convincingly set out. His philosophy, based on the ideas of four elements (earth, fire, air and water), the transmutability of matter and a living universe, formed the basis for an understanding of the natural world. In the context of this philosophy, experiments were conducted by alchemists. Their aims included the preparation of a universal solvent (*alkahest*), a universal medicine (*elixir*) and a transmuting agent, the philosopher's stone (*lapis philosophorum*), which would turn base metals into gold. This was perceived as a means of purification of the body and spirit of the alchemist. Whilst alchemists made much progress in the development of new apparatus, and separation and purification techniques, the results which they obtained were consistently unpredictable and therefore disappointing.

The 17th century witnessed a gradual, but radical change of approach to scientific experimentation. Matter started to be considered as non-living, and laws which governed its behaviour were now interpreted in terms of the physical parameters of the universe. There was, accordingly, a colossal growth in the number and variety of experiments and, more importantly, the interpretation of their results. Experiments were carefully designed, which involved specially constructed apparatus. Accurate and quantitative observations led to improved predictability of results.

The subject matter of this essay is concerned with one extraordinary success story of the new approach - the invention of the electric battery. Of particular interest are two phenomena: metals changing into other metals - chemistry, and the action of invisible forces - physics.

Changes in metals

Seven metals were known to the Ancients: gold, silver, copper, mercury, tin, iron and lead. Apart from gold which only occurs in the native state, most of the other metals were chemically extracted from their ores through the use of furnaces. As techniques for the mining of ores and the extraction of metals evolved, so a body of practical knowledge about metals was built up. Mineral acids such as sulphuric and hydrochloric were known in the Middle Ages, as were the salts of metals. Salts could be made by reacting metals with acids. The reactions of metals with salts of other metals were also known. The most striking of these was the reaction between iron (grey) and blue vitriol (copper sulphate solution), to yield copper (brown) and green vitriol (iron sulphate solution). Figure 1 shows: a) a sheet of mild steel [iron], b) copper sulphate solution, c) the sheet of steel immersed in the copper sulphate solution, d) the steel after half an hour.

This and other displacement reactions were described by the Bohemian metallurgist and assayer Lazarus Ercker [c. 1530-1594] in his celebrated book "Treatise describing the foremost kinds of metallic ores and minerals" (1574): "I wish to tell the reader that for a long time it was my belief that, since iron precipitates copper from copper solutions such as vitriol, green used argol, and the like, it is only the copper in such solutions that is precipitated by the iron and that the iron itself does not change into copper" [2]. We can

deduce that Ercker clearly did not believe in the possibility of transmutation. The aims of this book were entirely practical - they were devoid of philosophical speculation.

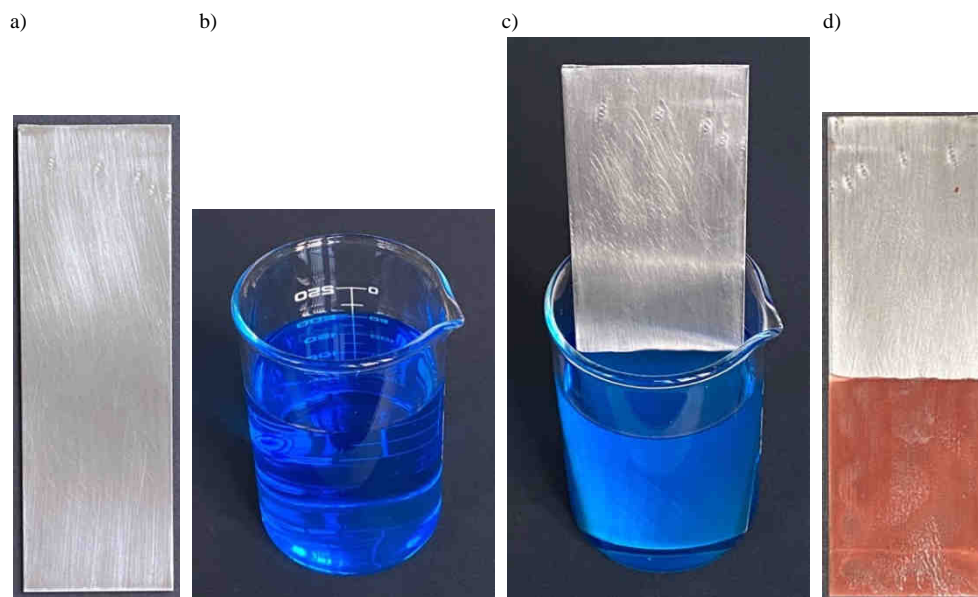


Fig. 1. a) Mild steel (iron), b) copper sulphate solution, c) steel immersed in the solution, d) steel partially coated with copper after reaction with the solution

The Polish alchemist Michael Sendivogius [1566-1636], secretive author of one of the most widely read alchemical texts, “De Lapide Philosophorum Tractatus Duodecim” (Prague, 1604), subsequently known as “Novum Lumen Chymicum” [3], wrote a chapter on metals and their reactions. The Ninth Treatise is entitled: “On the Commixion of Metals, and the Eliciting of their Metallic Seed”. He had clearly experimented with metals and their compounds, and was thus familiar with the reaction between iron and blue vitriol, which he described in typical alchemical language: “Consider also that the vertues of the Planets do not ascend, but descend: Experience teacheth us much, *viz.* that of Venus, or copper is not made Mars, or Iron, but of Mars is made Venus, as being an inferior sphere” [4]. However, unlike Ercker, Sendivogius compared the relative ease with which different metals were precipitated by reaction with salt solutions, and thereby established an order of relative reactivities. He used alchemical terminology, in which metals were denoted by planets and changes were explained by movements across planetary spheres. An interpretation of Sendivogius’ writing on metals shows that he gave a sequence of reactivities of metals which is in agreement with today’s electrochemical series [5].

A knowledge of the reactions of metals with salt solutions of other metals, and the relative reactivities of different metals had thus become well established by the beginning of the 17th century.

Invisible forces

Since early times, three types of invisible force have been recognised: electric, magnetic, gravitational. They manifested themselves in the form of: (i) electric attractions between amber (a fossilised golden coloured resin, known as “elektron” in Ancient Greece) and small pieces of dry organic matter such as straw, hair, feather, wool, chaff. (ii) magnetic attractions between loadstone (a black mineral, today known as magnetite, Fe_3O_4) and iron. This type of invisible force had been used to make magnetic needles for navigation purposes, by the Greeks and Chinese, some 2000 years ago. (iii) gravitational forces between bodies by virtue of their mass. These had been known and investigated by natural philosophers in the Ancient Greek, Indian and Islamic worlds for over two millennia. Galilei Galileo [1564-1642] and Isaac Newton [1642-1726] laid the foundations of mechanics, partly inspired through their study of gravitation.

The English natural philosopher William Gilbert [1544-1603], who conducted numerous experiments, wrote about magnetic forces in his “De Magnete” (1600). Although the main part of the book is concerned with magnets and magnetic forces acting in Earth, chapter two is entitled: “On the magnetic coition, and first on the attraction of amber, or more truly, on the attaching of Bodies to Amber”. Gilbert noted that in addition to amber, other bodies could be electrified by friction i.e. by stroking or rubbing. These bodies included glass, sulphur, sealing wax and diamond. He also noted that the electric force was affected by moisture, that hot or burning bodies lost all electricity and that an electric body attracts a variety of other bodies. A magnet by contrast, only attracts steel or iron. He thus clearly distinguished between magnetic forces and electric forces, and attempted to explain the difference: “Bodies are borne towards electricks in a straight line towards the centre of the electric; a loadstone draws a loadstone directly at the poles only...” and “Electrical motion is a motion of aggregation of matter; magnetical motion is one of disposition and conformation” [6].

Interestingly, both Sendivogius and Gilbert laid great stress on the importance of experiments, and they both scorned the opinions of scholastic philosophers.

Sparks and shocks

Unexpected and violent shocks have been experienced in a variety of circumstances by humans since time immemorial. Of specific note were the shocks caused by lightning and amphibious creatures. Aristotle had been intrigued by the torpedo fish, which was able to inflict a severe shock on someone attempting to catch it. Eels had also been known to give shocks, but the nature of the invisible forces which caused them remained unknown.

During the 17th century machines were invented for producing electric forces, which led to bigger and more dramatic shocks on bodies - both living and dead. This in turn led to the development of devices which could store the electricity - these were to become the first electric batteries.

Apart from the sheer fascination of studying these electric effects and how they affected organisms, practical applications of the machines were attempted e.g. for the treatment of paralysis and certain heart conditions.

The German natural philosopher, physicist and inventor Otto von Guericke [1602-1686] made two scientific sensations - the first was his demonstration of the magnitude of atmospheric pressure with his celebrated “Magdeburg hemispheres” experiment. The second, less known achievement, was his invention (in 1660), of

an electric machine. Its main feature was a globe of sulphur - a most unusual material which had in the past shown exceptional electric properties. To make the globe, he filled a glass phial the size of an infant's head with powdered sulphur, then heated the phial until the sulphur melted - it has a relatively low melting point of 113 °C. As the volume of liquid contracted, he topped it up with powdered sulphur, and broke the glass sphere once the sulphur had cooled and set. This was a smelly, dangerous, and by no means simple process! The sulphur globe was fixed by means of an iron axle to a wooden frame. As the globe was rotated, Guericke placed his hand on it as a rubbing medium, and it produced an electric charge which was much greater than that which had been achieved by rubbing pieces of amber with cloth or fabric. He caused a variety of extraordinary effects with this - it attracted many light objects such as leaves and retained them when it was rotated. Feathers and linen threads were made to hover in air, sparks were generated, crackling was heard, the globe became warm, and even glowed in the dark. Figure 2 shows Guericke's sulphur ball machine. This is part (Fig. V) of a larger illustration, *Iconismus XVIII*, which shows 5 other scientific experiments [7].

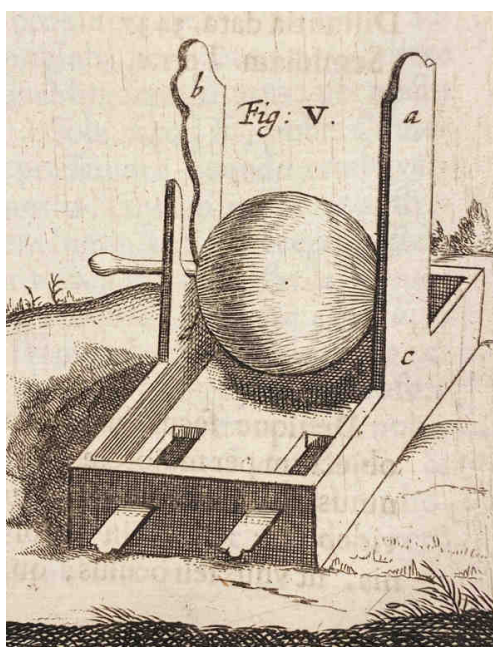


Fig. 2. Otto von Guericke's sulphur ball - the first electric machine [7] (courtesy of the British Library)

Such was the impact of the spectacular effects of the rotating sulphur ball, that they inspired a whole range of new apparatus which was developed for causing even more spectacular effects.

More efficient friction machines were subsequently invented. One was made by Professor (of theology) Andreas Gordon [1712-1751] - he replaced the sulphur globe with a glass cylinder. Another, using a glass disc, was invented by Professor (of philosophy and

philology) Johann Winkler [1703-1770]. Modern, even better frictionless electrostatic devices include the Wimshurst machine (1886) and the van der Graaf generator (1929).

Electrostatic experiments had their heyday in the world of science, from the 1740s onwards. Large scale demonstrations involving shocking effects with these machines became widescale. The demonstrations used to include the administering of shocks to large groups of people holding hands, small animals, and the use of sparks to ignite gunpowder and flammable liquids such as alcohol.

Yet progress in understanding the action of invisible electric forces was slow. It wasn't until the years 1733-1739, that the French physical scientist Charles du Fay [1698-1739] published results of experiments from which he announced the discovery of two kinds of electricity (vitreous and resinous), and two types of substances - electrics (conductors) and non-electrics (insulators). He made his deductions on the basis of observations of bodies attracting or repelling one another and their ability to hold charge. He noted that a glass rod would develop an opposite electric charge to a rod made of gum resin, if rubbed with the same material. Like charges repelled and unlike charges attracted one another: non-electrics (e.g. resin, sulphur, glass) could hold a charge whereas electrics (metals) would not hold a charge. Different rubbing materials e.g. cotton, silk, fur, could produce different types of electricity in the same rod. It was also noted that all apparatus had to be bone dry in order for effective build-up of electric charge and that when the charge was released, there was an accompanying spark which could generate a considerable shock. Du Fay naturally tried to explain his results, and he formulated a theory that electricity existed in the form of two fluids. This theory was subsequently replaced by that of the American polymath - writer, scientist, inventor, statesman, diplomat, publisher - Benjamin Franklin [1706-1790], who suggested that electricity was one kind of fluid, but that it could have two different charges.

Recognising the potential for applications of this new type of energy - today known as static electricity, scientists attempted to devise methods for capturing it and storing it - these were early forms of an electric battery. The Leyden jar was such a device, and it was invented independently by the Dutch scientist Pieter van Musschenbroek [1692-1761], of the University of Leiden in 1746, and the German jurist, Lutheran cleric, and physicist, Ewald Georg von Kleist [1700-1748] in 1745. The reasoning behind the invention was that it might be possible to collect electric fluid in a jar, in the same manner that water can be collected. Using false premises (electricity is a fluid) and false logic (electricity can fill a jar in the same way that water can), the scientists achieved their goal! The glass jar, which is an insulator, is coated with metal foil on the outside, and on the inside. A brass rod with a metal ball on top is fixed to the jar by an insulating material such as cork. The bottom of the brass rod has two wires protruding from it, which make an electrical contact with the metal foil inside. The jar, which had to stand on a conducting surface (earth) could be charged by inducing electricity, from a rotating sulphur ball or Wimshurst machine for example, into the brass ball. It would discharge by connecting the ball to the outer metal foil. Upon release of the stored energy, a spark of great intensity could be produced. Figure 3 shows a diagram of a Leyden jar being discharged [8]. Today, the Leyden jar has evolved into one of the most widely used electric components - the capacitor.

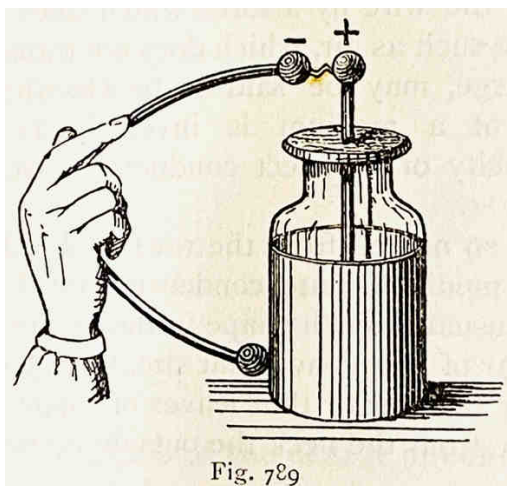


Fig. 3. Discharge of electricity from a Leyden jar [8]

Animal electricity

The torpedo fish, which had been known since antiquity to give severe shocks, became the focus of experimental investigation during the 18th century. In 1714 the French mathematician, natural historian and entomologist René Reaumur [1683-1757] studied the torpedo fish in some detail. He attributed the origin of its shocks to the muscles of the fish's tail, which had an unusual structure. In 1772 however, the English scientist and politician Dr John Walsh [1726-1795], who had developed a specialist interest in "shocking" fish and did some experiments with them, attributed the torpedo fish shocks to electricity [9]. He was unable to explain the origin of the electricity but is today considered to be one of the first European neuroscientists [10]. His work prompted much further research and helped to bring the issue of electricity in animals to the forefront of scientific endeavour. The English natural philosopher Henry Cavendish [1731-1810], best known for his work on hydrogen, also experimented with the torpedo fish, and attempted to explain the origin of its electricity [9].

Towards the end of the 18th century, despite many experiments involving dissections and detailed examinations of torpedo fish anatomy, no-one was able to provide a satisfactory answer to the most perplexing question: what causes this form of electricity?

Luigi Galvani [1737-1798] was an Italian physician and natural philosopher. As a child he developed a strong interest in science, focusing particularly on biology and medicine. He specialised in surgery as part of his medical degree and was appointed lecturer in anatomy at the Academy of Sciences at the Institute of Bologna in 1775. His wife Lucia Galeazzi, who was the daughter of one of his professors, worked with him on several projects, and actively participated in his experimental research. This spanned several years, hundreds of experiments, and gave birth to many ideas. He discounted the idea that muscle twitching could be caused by induced electricity from an electrostatic machine (artificial) in the vicinity of the animal, or by atmospheric electricity (natural). Galvani also believed that, unlike Volta, this electricity could be made to flow in the bodies of both living and dead animals.

A breakthrough came in 1780. Having noted the influence of electricity on the nervous excitability of animals, especially frogs, Galvani observed that when the lumbar nerves of a dead frog were connected with the crural muscles by a metal conductor consisting of two different metals e.g. copper and zinc, the muscles were briskly contracted. From these observations, Galvani concluded that the twitching of the legs was caused by a type of electricity, which was generated in the frog's muscles. He thought that this was a form of animal electricity. Figure 4 shows Galvani's experiment [8].

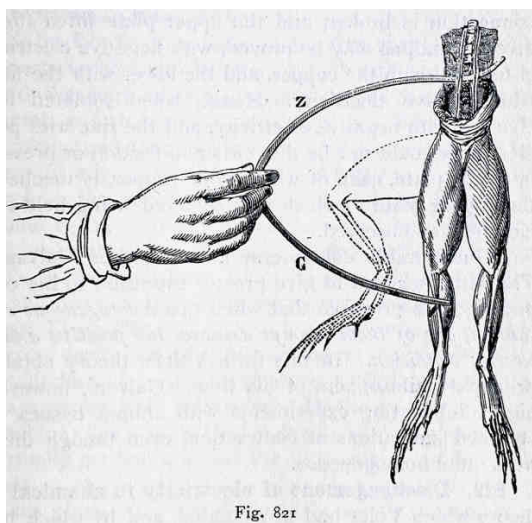


Fig. 4. Galvani's twitching frog's legs experiment [8]

Galvani believed that the electricity, which he called a *vital fluid* that was inherent in the animal, passes from the nerves of the muscles by the metallic arc, and was thus the cause of the contraction. He published the results of his extensive research in 1791 in a book entitled: *De viribus electricitatis in motu musculari commentarius* (*Commentary on electric forces in the movement of muscles*). Although his cleverly and painstakingly construed theory was initially widely accepted in scientific circles, it was not without opponents.

Chemical electricity

No person's name is as universally known in the world today, as that of the Italian physicist and chemist Alessandro Volta [1745-1827]. The standard unit of electric potential, the Volt, was named after him in honour of his invention of the electric battery. Alessandro was born in Como in Italy, into a family which was at the milieu of cultural and social activities. Education, philosophy, music, art, science and religion were central to the world in which Volta grew up. There was some pressure on him from his family to enter the priesthood, and with this aim in mind, in 1761 he entered the Benzi Seminary, Como. While studying there, Volta was encouraged by a family friend, Canon Giulio Cesare, to develop his interest in a field of study which was very much in vogue at that time - experimental physics - electricity. It was in this direction that Volta's life was to evolve.

At the age of 24 he published a treatise entitled: *On the forces of attraction of electric fire*. In 1774, at the age of 29 he was appointed professor of physics at the Royal School in Como and in 1779 he became professor of experimental physics at the University of Pavia. He held this post for 40 years.

Volta had also developed a strong interest in chemistry. Between 1776 and 1778 he devoted some time to the chemistry of gases, a field of inquiry that was also rapidly evolving at that time. In November 1776, having read a paper by the American scientist Benjamin Franklin on “flammable air”, Volta isolated methane gas from decomposing organic matter at the edge of Lake Maggiore. He identified this as a chemical substance and is thus credited with its discovery. Naturally the flammability of methane fascinated him the most and using his excellent practical knowledge of how to store electrical energy and discharge it to cause a spark, he devised a method for igniting methane with a spark. Today this method forms the basis for gas ignition in a multitude of applications, including internal combustion engines and piezo-electric lighters.

When Volta read Galvani’s work on the frog’s legs experiment, he was initially impressed with the idea that electricity originated in muscles. He had a hunch however, that this might not be the case, and that perhaps it was the contact of two dissimilar metals with a moist surface that was the cause? He experimented with different pairs of metals on his tongue and eyeballs and discovered that they caused a tingling sensation. He also noted that when the most reactive metal was paired with the least reactive one, would provide the greatest sensation. From these observations he reached the conclusion in 1794, that electricity was generated from the contact of two metals with a saline solution, and not from muscles. This was to become the main thrust of his theory. Simply put, it stated that: electricity is metallic, not animal. At the same time as he published his new theory, Volta completed the design of the battery so that it could be more widely used.

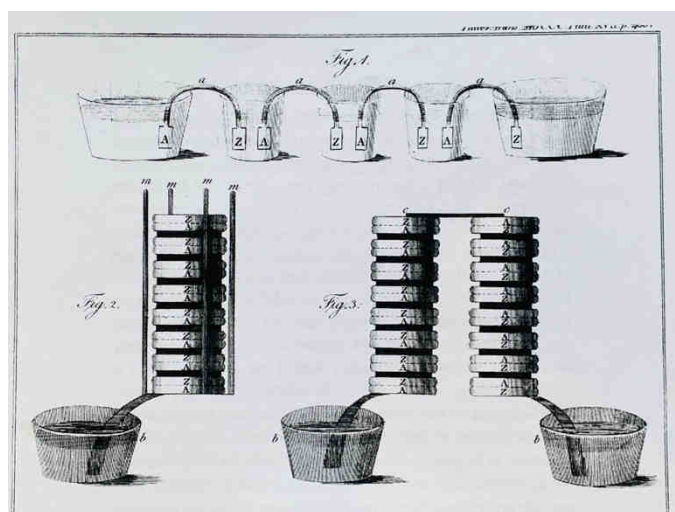


Fig. 5. Volta’s “couronne des Tasses” and his electric piles with electrodes dipping into basins of saline solution [1]

Yet he was aware of many shortcomings of the electric pile: it had a short life when in use, the weight of the metal discs squeezed out the saline solution from the cloth discs thus reducing moisture content and hence the capacity of the battery to deliver a shock. He overcame the weight problem by arranging the cells in a “couronne de tasses”, or “crown of cups”, as he called it. It worked very well, giving significant shocks to his body, but was bulky and fragile. He also constructed a cage for the discs - the top and bottom was made of wood, with metal rods, carefully insulated, providing the frame. This construction became known as Volta’s pile. He also suggested practical applications of the battery for: anatomy, psychology and general medical practice. Figures 5 [1] and 6 [8] show the two types of arrangement of metals in the battery, and its actual construction.

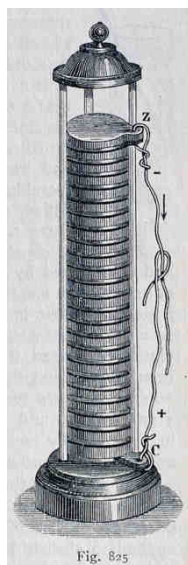


Fig. 6. Volta’s pile, arranged in the form of a functional battery [8]

Electric sparks, which had been studied for the previous 150 years, released their energy in a fraction of a second. Volta’s new form of electricity could, however, be drawn over a period of time. Today it is called current electricity, to distinguish it from sparks, which are released during the discharge of static electricity.

Although it was not until 1807 that the English chemist, populariser of science and inventor Humphry Davy [1761-1829] proved that chemical changes were the basis for the release of electricity in the Voltaic battery, it nevertheless heralded the new the age of chemical electricity.

When Volta published his paper in 1800, he immediately became a scientific celebrity. The effect of producing electricity was sensational because of the remarkably simple manner in which this energy could be released - no mechanical effort - just small plates of two different metals, arranged alternately in a saline solution, with two wires protruding. It came as no surprise then, that this battery immediately caught the imagination of scientists. Their experiments led to unprecedented chemical and physical effects.

In 1800, a spectacular chemical effect was achieved by the Englishmen, chemist William Nicholson [1753-1815] and surgeon Anthony Carlisle [1768-1840]. They used Volta's battery to electrolytically decompose water into hydrogen and oxygen. In so doing, they had not only become the first people to decompose water directly into its elements (thus verifying that it is a compound of these two elements) but they had also initiated the new sister discipline of chemical electricity, Electrical Chemistry, or electrolysis. Interestingly, Nicholson, who was a prolific experimenter and active correspondent of Volta, and the Italian natural philosopher Tiberius Cavallo [1749-1809], had been the only two persons who were mentioned by Volta in his paper [1].

Concurrently with initial successes with Volta's pile there began a process, which lasts to this day, to improve the efficiency of the battery. This involved a wide range of design criteria: power (maximum electromotive force [EMF] and minimum internal resistance), size, weight, consumption of raw materials in its construction and usage, ease of usage, ease of manufacture, portability, durability, ease of recycling. Connected to the utilitarian aspects of chemical electricity, there opened up a whole new field of research, beyond the science and technology of batteries. This concerned the understanding of matter and its interaction with energy.

Two fields of inquiry - practice and theory - have thus evolved since Volta's invention of the electric battery. Some notable achievements are discussed in the context of timelines.

Timeline: Practical development of cells

The disadvantages of early electric cells included: (i) they contained liquids which were corrosive and easy to spill, (ii) they became quickly discharged, (iii) their EMF output was not constant, (iv) polarisation - accumulation of gas bubbles, which reduced the output voltage of the cell, (v) they were heavy, cumbersome and fragile.

1802 - William Cruickshank [c.1740 - c.1811] developed the horizontal (trough) battery, which was easily portable, unlike Volta's vertical battery. It employed zinc and copper electrodes, with an electrolyte of dilute sulphuric acid. Figure 7 shows a diagram of the battery [11].

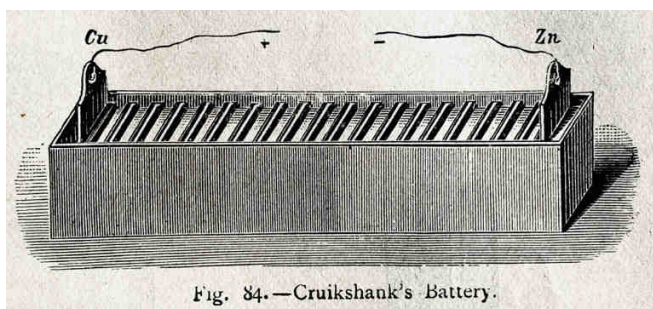


Fig. 7. Cruickshank's trough battery [11]

It played an important role in some extraordinary experiments whose aim was to produce the most extreme effects of a given phenomenon. One of these was a short pulsed arc of extremely bright light, between two carbon electrodes, which Humphry Davy had briefly created in 1800.

In 1802, independently of researchers in West Europe, the Russian experimental physicist Vasilii Petrov [1761-1834] built an enormous battery of 42,000 cells and used it to produce the first carbon arc light [12].

In 1808, Humphry Davy used 30 Cruickshank batteries, wired in series, to electrolyse molten salts and isolate the alkali metals sodium and potassium. These batteries had a short life span, and in the same year, he ordered a giant battery, composed of the newly developed Wollaston cells, to be built at the London Institute (a short distance from the Royal Institution) so that he could use it for public demonstrations. Construction of the battery, which cost £1000, took 5 years. When completed, it consisted of 2000 cells, which took up 889 square feet (83 m²) - almost the entire area of the Institute basement.

1808 - William Wollaston [1766-1828] designed an improved version of Cruickshank's battery - it was much more powerful. In each cell, the zinc plates are kept centrally adjusted by wooden spacers between the halves of a doubled copper plate bent round under them. The whole set of plates, which was connected by strips of copper, was attached to a wooden frame. This could be easily lifted out, thus stopping any reaction. Figure 8 shows the arrangement of cells in this battery [11].

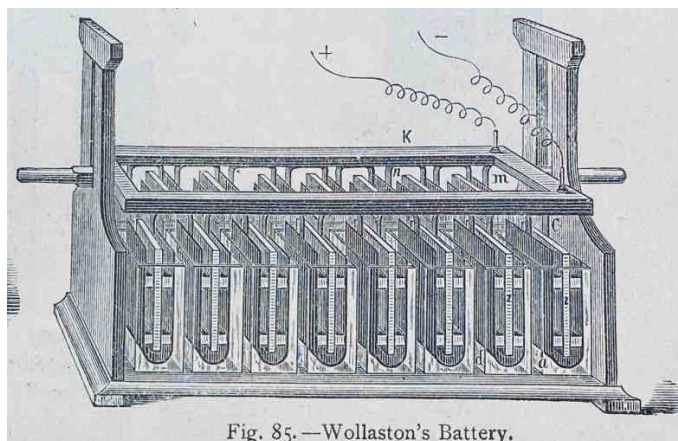


Fig. 8. The arrangement of cells in Wollaston's battery [11]

Figure 9 shows a scene depicting Humphry Davy in 1813, demonstrating his brilliant carbon arc, probably at the London Institute, where he gave public lectures. Scientists and members of the public were delighted, shocked and intrigued with the intensity of the light which could be produced. They were witnessing remarkable energy transformations for the first time: chemical to electrical to light. The long shadow cast by Davy's body emphasises the brightness of the arc discharge.

1836 - As a young man, John Daniell [1790-1845] became inspired to develop an interest in science through his contacts with the scientific milieu of the Royal Institution. In 1813, aged only 23, he was appointed professor of physics at the University of Edinburgh and in the following year he was elected a fellow of the Royal Institution. Among his many friends there was Michael Faraday, who had already established himself as an outstanding experimenter. Faraday was particularly interested in electrochemistry and challenged Daniell to design a voltaic battery with improved reliability. Daniell accepted

the challenge, and solved the problem of polarization by designing a cell in which hydrogen was eliminated during the generation of electricity. The cell consisted of a copper can filled with copper sulphate solution, in which was immersed a porous earthenware container filled with zinc sulphate solution and a zinc electrode. It gave a constant EMF of 1.1 V over a long period of time. Figure 10 shows an historic photograph, taken at the Royal Institution in about 1840, of John Daniell with Michael Faraday. A battery of Daniell's cells is seen on the table.

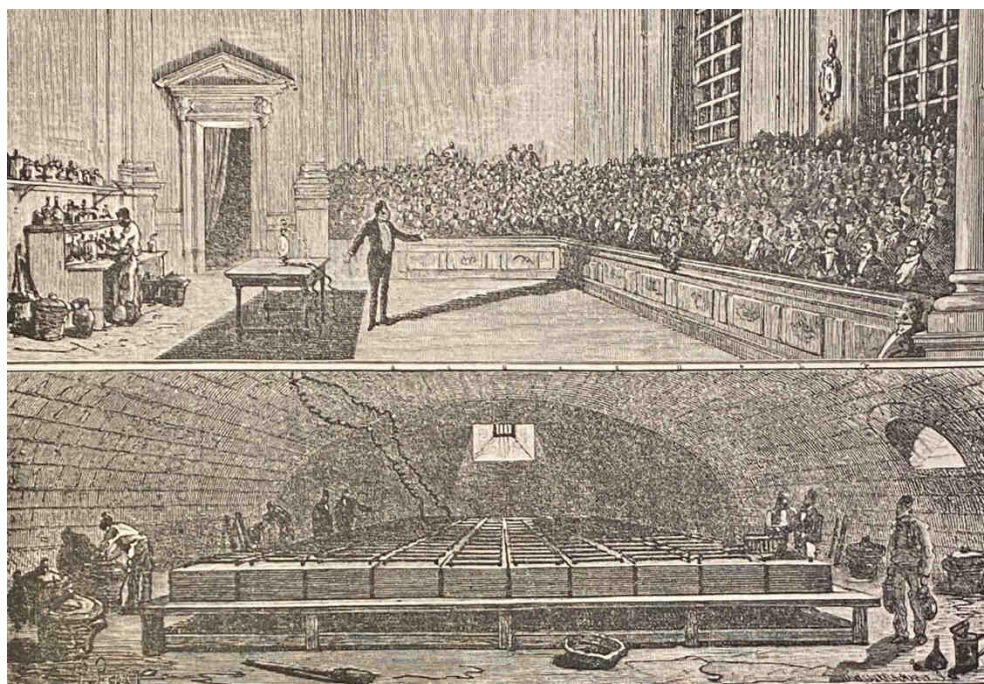


Fig. 9. Humphry Davy demonstrating a carbon arc light at the London Institute in 1813, and below, probably in the basement of the London Institute is the 2000 cell "Great Battery" (courtesy of the Royal Institution archive)

Daniell cells provided a reliable source of electricity and were extensively used for telegraphy - an early form of telecommunication - from about 1840, and for electroplating with metals. They played a key role in the rapid growth of the Anglo-American telegraph network during the 1840s.

1842 - The first fuel cell, called a gas voltaic battery, was invented by William Grove [1811-1896]. During the 1830's, Grove had experimented with the idea of using liquids to form voltaic cells. Although he achieved a measure of success, the gases produced during their use, the oxides of nitrogen, were toxic. Grove overcame the issue of toxic gas release, by designing a cell which did not involve toxic chemicals. This had been inspired by Cruikshank's electrolysis of water which gave hydrogen and oxygen as its gaseous products. A further key inspiration for this battery came from the recently discovered fact that platinum, coated with platinum black, has an outstanding capacity to adsorb gases on

its surface. The cell could produce an EMF of about 1.5 V. It works on the principle that when a current is drawn, hydrogen and oxygen gases, present initially at electrodes A and B in the ratio 2:1, are converted to water. When no gases remain, the cell is full discharged. On recharging from an independent battery, the acidified water in the tubes is electrolytically decomposed into hydrogen and oxygen, and the cell will again produce an EMF. This was the first type secondary (rechargeable) cell. Limitations of this cell included its bulkiness, fragility and limited power output. Figure 11 shows a battery of 4 Grove cells [8].

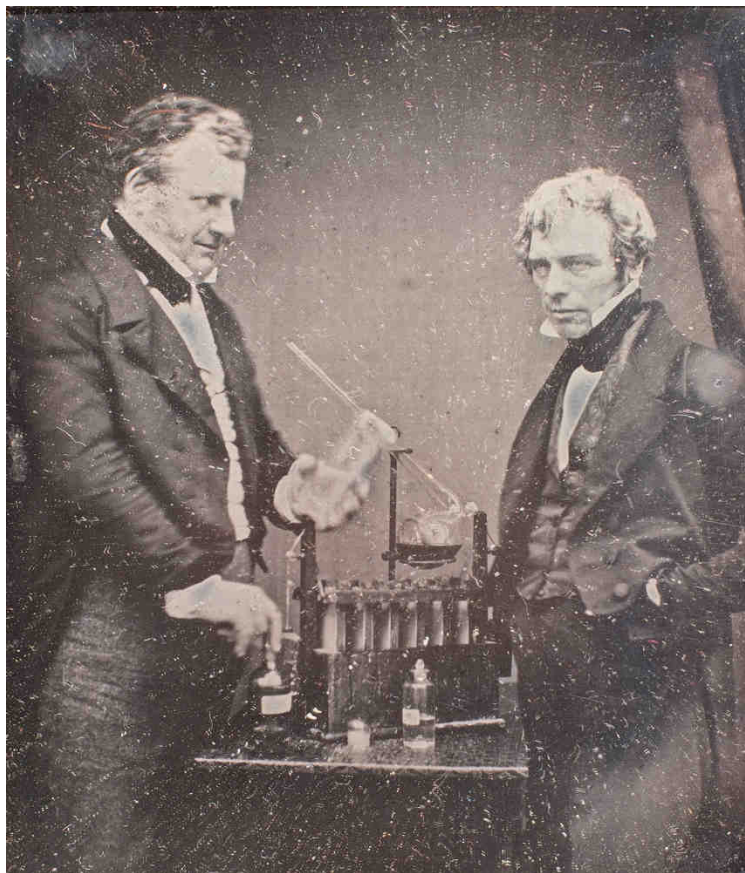


Fig. 10. A Daguerreotype (early form of photograph) showing John Daniell with Michael Faraday c.1840 (courtesy of the Royal Institution archive)

1859 - The idea of an easily rechargeable battery, which was portable, compact and could also store electrical energy for some time, was a major issue in battery design. Gaston Planté [1834-1889] achieved a significant breakthrough in electric cell chemistry, with his invention of the lead/acid battery. This cell could also provide a high current surge, on account of its low internal resistance.

Invented 160 years ago, it was the precursor to today's lead/acid batteries which continue to constitute the world's most popular form of electrical energy supply for cars with internal combustion engines.

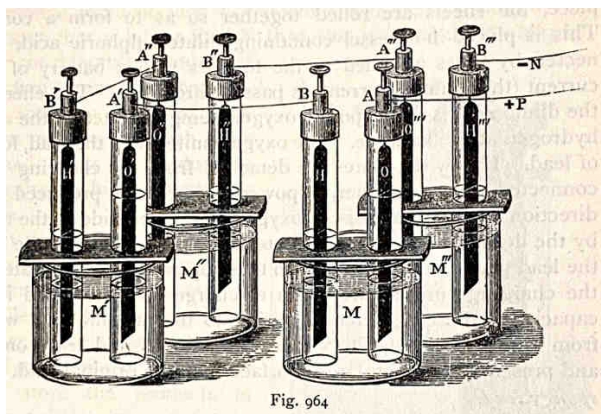


Fig. 11. A Grove gas voltaic battery, consisting of 4 cells [8]

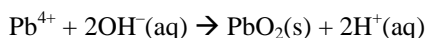
Figure 12 shows a home-made lead/acid battery, which illustrates its principle i.e. reversibility, and is suitable for teaching purposes. Each of the jars contains 30 % sulphuric acid, and the electrodes are pieces of roofing lead, cut into suitable shapes. There is a white sediment of lead sulphate, which has built up while the battery has stood inactive for a few months. As the battery is charged, the anodes become coated with a dark brown layer of lead dioxide and bubbles of oxygen are evolved from them. This battery will cause a small car lamp to shine for a few seconds, before becoming discharged again. It can then be recharged.



Fig. 12. Home-made lead/acid battery, suitable for teaching purposes

The EMF is produced by the reaction between lead and lead dioxide, and not, as it would appear, between two lead electrodes. Several equations are required to describe the electrochemical changes which take place - some for charging and discharging the cathode, and some likewise for the anode. The essential feature which enables the recharging of the cell to occur is the chemistry of lead, and its ability to exist in two oxidation states. One of

these is Pb(II) in the Pb^{2+} ion, as in lead sulphate, PbSO_4 . This is the more common metallic, or cationic state. The other is Pb(IV), found in PbO_2 , lead dioxide. As an example, the process for charging the anode is briefly explained. Its purpose is to show how a layer of brown lead dioxide is formed on the anode, when it is initially charged. When lead is placed into sulphuric acid, it becomes coated with a microscopically thin layer of lead sulphate, which is virtually insoluble in water, but nevertheless releases a tiny number of lead ions, Pb^{2+} , into solution. When a charging current is applied, electrons are lost from the Pb^{2+} ions and they become oxidised to the +4 (IV) state: $\text{Pb}^{2+} \rightarrow \text{Pb}^{4+} + 2\text{e}^-$. As these ions are removed from solution, an equilibrium is disturbed, and more Pb^{2+} ions go into solution. The Pb(IV) then reacts with hydroxide ions which are present in water, to form lead dioxide and hydrogen ions.



1866 - Georges Leclanché [1839-1882] developed the wet cell, which was much lighter and safer (no sulphuric acid) than the lead/acid battery. This consisted of a zinc anode and a carbon cathode surrounded in a porous pot with a mixture of powdered manganese dioxide and carbon. The pot was immersed in a jar of ammonium chloride solution. This cell gave an EMF of 1.4 V. Figure 13 shows the arrangement of components in a Leclanché cell [11].

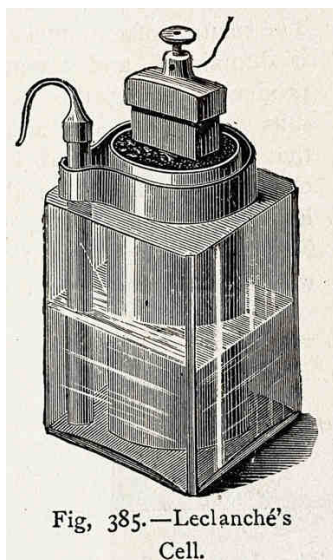


Fig. 13. The Leclanché cell [11]

1886 - Carl Gassner [1839-1882], who was an extraordinary man, invented the dry cell which used the same chemistry as the Leclanché wet cell, but which was much more portable, for it did not use a liquid [13]. The ammonium chloride was mixed with Plaster of Paris (calcium sulphate) to form a paste. The carbon cathode, surrounded by powdered compacted manganese dioxide/carbon, was immersed in this paste and both were sealed in a zinc shell which acted as the anode.

1899 - Waldemar Jungner [1869-1924] invented the NiCd battery. This was a rechargeable battery, which was lighter than lead/acid batteries, and was the first battery to employ an alkaline electrolyte (potassium hydroxide).

1967 - Detchko Pavlov [1930-2017] commences a long career in the development of lead acid battery chemistry and technology, which led to a significantly increased efficiency of lithium alloy batteries (LAB).

1980 - John Goodenough [1922-] made significant improvements to the lithium primary cells, which had been in use since the 1970's, by discovering the lithium cobalt oxide (LiCoO_2) cathode, and by using organic catalysts.

1991 - Akira Yoshino [1948-] built the first lithium-ion cell, which was a rechargeable and more stable (less prone to overheating) version of the lithium battery.

For their contribution to chemical electricity, Professors Goodenough and Yoshino were awarded the Nobel Prize for Chemistry in 2020.

Timeline: Theoretical developments

As a result of the “electrochemical revolution” during the first decades of the 19th century, a whole new range of questions arose. These concerned two interrelated fields of inquiry: (i) electric potential and current electricity, (ii) the nature of matter and its relation to energy. Some of these questions are listed below:

(i) How is the electric potential between two different metals established? Why do different pairs of metals give varying levels of electricity? Can substances other than metals be used? How can the electricity be measured? What actually does an electric current constitute? Why do different metals give different levels of electricity? How does temperature and concentration of the electrolyte affect the level of electricity, and why does this happen? Is the electricity generated by a battery the same as that generated by a spark?

(ii) What kind of particles are present in water, metals and in solutions of their salts? How do these particles acquire an electric charge, and how do they lose it? What happens to the particles when a current flows - how do they move and how do they change? How do particles combine to make new substances? What sort of forces hold particles together? What is electricity?

At the beginning of the 19th century some new important ideas about matter had been accepted by the scientific community.

Matter was considered to be made of tiny particles - atoms and molecules. These could exist in different forms, depending on the state of aggregation of the particles: solid, liquid, gas. As the temperature of a substance was raised, so the particles gained more energy and moved faster; accordingly, their state could change. Ideas such as these formed the basis of the kinetic theory of matter which gradually evolved into the growing field of thermodynamics, during the second half of the 19th century.

In 1808, the English natural scientist John Dalton [1766-1844] published his Atomic Theory, which among other ideas, stated that atoms are indestructible and indivisible. Although the theory was widely accepted, it did not explain how atoms combine to form compounds. This raised the issue of chemical affinity i.e. how are atoms attracted to one another during a chemical process, and what happens to them once they have become part of a compound? How are chemical bonds formed? Electrochemical experiments which utilised the concept of ions played a significant role in providing answers to these questions.

The following timeline gives a brief overview of some important advances which were made in electrochemistry.

1805 - The German/Lithuanian chemist Theodor Grotthuss [1785-1822] devised a theory to explain the newly discovered phenomenon of the electrolysis of water. He suggested that the water molecules are polar, with positive and negative ends. When an electric field was applied, the molecules lined up in a chain. If the strength of the field was large enough, the ends of the molecules which are near the electrodes are pulled from the molecule and deposited at the electrode. Thus hydrogen was released at the negative terminal and oxygen was released at the positive terminal. The remaining bits of molecules (now charged) at the end of the chains would then join up with adjacent molecules in a process which could be described as charge transfer. The “new” molecules would then flip over, and the process would begin again. Although this theory had several drawbacks, it played a key role in the development of electrochemical theory during the 19th century. The idea of charge transfer has today been extended to explain proton mobility in biological systems, fuel cells and energy storage processes [14].

1807 - The English chemist and inventor Humphry Davy [1778-1829] recognised that *chemical reactions* occur within the cells during the discharge of an electric current. In doing so he defined the science of electrochemistry. Furthermore, he defined the two fields of electrochemistry: chemical electricity - the generation of an electric current from a chemical reaction, and electrical chemistry (electrolysis) - the decomposition of a molten liquid by passage of an electric current. He tried to explain electrochemical changes and advanced a theory of chemical affinity which explained how opposite charges were attracted to one another during electrolysis.

1834 - In addition to his ground breaking work in the field of electromagnetism and the invention of the electric motor, the English natural philosopher and inventor Michael Faraday [1791-1867] formulated the laws of electrolysis, which was the first quantitative work in this field. He also introduced the concept of electrically charged particles, which he called ions. However, he was unable to offer a satisfactory explanation of how ions were formed from their atoms e.g. how is a sodium ion formed from a sodium atom? He also introduced the terms: electrode, electrolyte, cathode, anode, cation, anion. Faraday was an outstanding educator and populariser of science [15].

1853 - The German physicist Johann Hittorf [1824-1914] invented the concept of transport numbers. He defined the transport number of a given ion as the ratio of current carried by that ion, to the total current flowing during electrolysis. For this purpose, he ingeniously devised porous partitions for the electrolysis experiments. During the electrolysis of 0.01M NaCl(aq) at 298 K for example, values of 0.3918 for Na⁺, and 0.6082 for Cl⁻ have been calculated [16]. Hence Cl⁻, having the larger value, moves faster than Na⁺ during the reaction - it is said to have a higher ionic mobility.

1875 - During the period 1869-1880, the German physicist Friedrich Kohlrausch [1840-1910] and his co-workers published a long series of papers on the results of their careful investigations of the electrical conductivity of aqueous solutions of ionic compounds. To ensure supreme accuracy, Kohlrausch used water, which had been distilled 42 times in vacuo. The measurements were made over a range of pressures, temperatures and concentrations. His law of independent ionic mobilities states that: *At infinite dilution, the ionic mobilities are independent. Thus the equivalent conductance of an electrolyte is the sum of the separate ionic mobilities.* The concept of infinite dilution is naturally a difficult one to grasp, and values of any property at infinite dilution can only be obtained

by extrapolation of a relevant graph. From a table of independent ionic mobilities, it is possible to calculate the equivalent conductance at infinite dilution of weak electrolytes. This would not be possible from experiments.

1884 - In 1903, the Swedish physical chemist Svante Arrhenius [1889-1927] was awarded the Nobel Prize for chemistry, for "his theory of electrolytic dissociation". He published his theory as part of his PhD thesis, which was submitted at the University of Uppsala in 1884. There were considerable obstacles in accepting his novel idea: a molecule, which is electrically neutral, can split into ions. Nevertheless, with time it became clear that this was indeed the case. Arrhenius extended his ideas on ions to define an acid as a substance which furnishes an excess of hydrogen ions in aqueous solution, whereas an alkali furnishes an excess of hydroxide ions. This enabled the chemistry of reactions in aqueous solutions to be much better understood.

1889 - The German physicist Walther Nernst [1864-1941] was a key scientist in the development of chemical thermodynamics. He was awarded the Nobel Prize in 1920 for chemistry for his work on thermochemistry. He formulated an equation from which the EMF of a cell could be predicted, on the basis of the concentrations of ions in the electrolyte. This was the most basic equation in equilibrium electrochemistry. This EMF is given as:

$$E = E^{\circ} + RT/zF \cdot \ln [\text{oxidised form}]/[\text{reduced form}]$$

where E is the predicted EMF, E° is the EMF under standard conditions, R is the universal gas constant ($= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature [K], F is the Faraday constant ($9.648 \cdot 10^4 \text{ C} \cdot \text{mol}^{-1}$), z is the magnitude of the cation charge, $\ln[\text{ion}]$ is the natural logarithm of the ion concentration [$\text{mol} \cdot \text{dm}^{-3}$].

Until recently, this equation formed the basis for excellent school experiments [17].

1893 - The quantification of chemical phenomena has played a key role in the elevation of chemistry to an exact science. It is not surprising therefore, that as soon as Volta's battery had been demonstrated, there would be a demand to assign a number to represent the electric effect. This number, a measure of electric potential, became known as the Volt. In 1820 the Danish physicist Hans Christian Oersted [1777-1851] conducted an epoch making experiment, in which he showed that a wire which was carrying an electric current could deflect a magnetic needle. In this way he established a direct link between the two invisible phenomena - electricity and magnetism. Subsequently this effect of an electric current deflecting a magnetic needle was to form the basis for Voltmeters - the greater the potential difference across two points on a conductor, the greater the deflection of the needle. It was not until the middle of the 19th century that accurate voltmeters were developed. It was then that the idea was born, to construct a series of electrochemical reactions in order of the potential difference which they would generate. In order to be meaningful, this potential difference, expressed in volts, would have to be measured under standard conditions (temperature, pressure, concentration of electrolyte), against a standard electrode. It was the German chemist Max Le Blanc [1865-1943] who invented the standard hydrogen electrode [18]. This was to play a key role in the establishment of the Electrochemical Series (table of standard electrode potentials), part of which is reproduced in Figure 14 [19].

Using such a table, it is possible to calculate the EMF of electric cells, and to predict the course of redox reactions which involve transfer of electrons.

Table 11.2. STANDARD SINGLE-ELECTRODE POTENTIALS

<i>Electrode</i>	$\pi_{298}^{\ominus}(\text{V})$	<i>Reaction</i>
Pt, K(Hg) K ⁺ (aq)	-2.92	K ⁺ + e ⁻ → K
Pt, Na(Hg) Na ⁺ (aq)	-2.71	Na ⁺ + e ⁻ → Na
Zn Zn ²⁺ (aq)	-0.761	Zn ²⁺ + 2e ⁻ → Zn
Pb Pb ²⁺ (aq)	-0.13	Pb ²⁺ + 2e ⁻ → Pb
Pt, H ₂ (1 atm) H ₃ O ⁺ (aq)	0.000	2 H ₃ O ⁺ + 2e ⁻ → 2 H ₂ O + H ₂
Ag, AgCl Cl ⁻ (aq)	+0.22	AgCl + e ⁻ → Ag + Cl ⁻
Pt, Hg, Hg ₂ Cl ₂ Cl ⁻ (aq)	+0.27	Hg ₂ Cl ₂ + 2e ⁻ → 2 Hg + 2 Cl ⁻
Cu Cu ²⁺ (aq)	+0.34	Cu ²⁺ + 2e ⁻ → Cu
Pt Fe ³⁺ , Fe ²⁺ (aq)	+0.77	Fe ³⁺ + e ⁻ → Fe ²⁺
Pt, Cl ₂ (1 atm) Cl ⁻ (aq)	+1.359	Cl ₂ + 2e ⁻ → 2 Cl ⁻

Fig. 14. Table of standard electrode potentials [19]

In 1896 J.J. Thomson [1856-1940] experimentally established the existence of particles which are smaller than atoms. These were named electrons. Further work on the structure of the atom by physicists Henry Moseley [1887-1915], Ernest Rutherford [1871-1937], James Chadwick [1891-1974] and Niels Bohr [1885-1962], led to today's model of the atom. Electrons are arranged in shells, or energy levels, around the nucleus of the atom, which consists of two additional types of particle: protons and neutrons. The number of electrons in the outermost shell, which are the most weakly attracted to the nucleus, determine the chemical characteristics of the element. Metals typically have 1, 2 or 3 electrons in their outer shells. During chemical reactions involving metals, these electrons are lost, resulting in the formation of cations with charges +1, +2 or +3. Electrochemical processes also exist, in which electrons can be lost from molecules or ions of non-metals. Examples of such systems are found in the table above e.g. H₂/H₃O⁺, Fe³⁺/Fe²⁺, Cl⁻/Cl₂. Electric cells are made from two half cells. Although metals are frequently used, the Grove cell (1842), mentioned earlier, involved oxygen and hydrogen gases for the production of an EMF.

When an electric cell has a current drawn from it, the outer electrons of the reacting species are transferred, and constitute the current. During this process, the metal atoms or ions/molecules, undergo a change, which results in the formation of a **new** chemical species. Hence the term: **chemical electricity**.

Conclusion

In 1936, the eminent science historian Frank Sherwood Taylor, wrote a prophetic statement:

"A great many batteries have been devised... If a really light and strong quick-charging storage battery could be devised it would revolutionise transport. The cars or vans fitted with it would ordinarily be left charging overnight: garages would have

arrangements to charge it up in five minutes or so. An electric motor driven by a battery is comparatively light: it gives tremendous acceleration and very little trouble. The danger of fire from petrol would be eliminated, and the noise and exhaust fumes of our streets would be halved. No gears would be needed on an electric car, for some motors pull even better at lower speeds than at high. If any of my readers wants a hundred million pounds, let him invent and patent a light, strong storage battery which can be charged in a few minutes. There is nothing theoretically impossible about it: but no one has yet found a way to do it" [20].

So today, 66 years later, a hundred million pounds is still up for grabs.

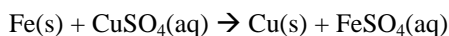
Appendix

The reaction between copper sulphate solution and iron lends itself most effectively for teaching important ideas in chemistry. These include: writing chemical equations - word, symbol and ionic, redox reactions, the Reactivity series and displacement reactions, electrode potentials, chemical analysis - testing for iron(II) and copper(II) in solution, transition metals - complex ions and coloured ions, energy changes in chemical processes - heat and electrical, crystallisation by evaporation, the chemistry of rusting.

Figure 15 shows the reaction, which can be simply represented by means of a word equation:

iron (grey) + copper sulphate solution (blue) →
copper (brown) + iron sulphate solution (green)

Using chemical symbols,



At an elementary level, this is explained as a displacement reaction in which the iron, being more reactive than the copper, displaces it from solution. In order to show this reaction effectively, it is necessary to use an excess of iron. Figure 14 shows a sequence of experiments which illustrates this effectively.



Fig. 15. The reaction of iron with copper sulphate solution - nos. 1-5 from left to right

Boiling tubes 2 and 3 contain 1M copper sulphate solution and coarse iron filings respectively. The solution is added to the filings and is shaken for 2-3 minutes. The blue colour is discharged and replaced initially by a murky green colour. The reaction is exothermic, liberating heat energy, which is shown by a warming (about 20 °C rise in

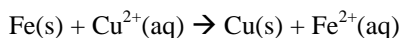
temperature) of the reacting mixture. If this tube is allowed to stand for a few hours, the murky impurities (from iron) will settle as a sediment on the iron filings, which are now coated with a brown layer of copper, and the resulting solution will have a pale green colour, typical of compounds containing Fe^{2+} (aq) ions. This is shown in boiling tube 4. To prove that the copper ions have been completely discharged from the solution, two further boiling tubes, containing 0.880 ammonia are placed at either end - 1 and 5. A few drops of the ammonia solution are added to both of these tubes. This is a very sensitive test for Cu^{2+} (aq) ions. The drops from tube 2 impart a brilliant blue colour to the ammonia - this is the copper tetramine complex ion, whereas the drops from tube 4 give a gelatinous green precipitate of $\text{Fe}(\text{OH})_2$, without a trace of blue in the solution.

As an extension of this experiment, the steel plate from Figure 1 can be left in the copper sulphate solution for a few days. In this situation, as the water evaporates from the solution, and the reaction proceeds to completion, crystals of iron(II) sulphate are observed. The effect is shown in Figure 16. The brown colour at the interface is caused by iron(III) oxide (rust), formed by reaction of iron with water, in the presence of air. There is no doubt that alchemists and early chemical technologists would have been familiar with this kind of effect, and many others like it. With hindsight, it is possible to understand, that this type of phenomenon, i.e. crystals growing, provided evidence for the idea of panvitalism, i.e. a living universe.



Fig. 16. Crystals of iron(II) sulphate, formed at the interface of mild steel reacting with copper sulphate solution

Once it had been established, late in the 19th century, that the particles responsible for this type of reaction are electrically charged ones called ions, the equation could be written in ionic form:



Finally, in the latter half of the 20th century, with the broader understanding of electron transfer during these reactions, they became classed as REDOX reactions. Accordingly, the above ionic equation can be written in two halves:

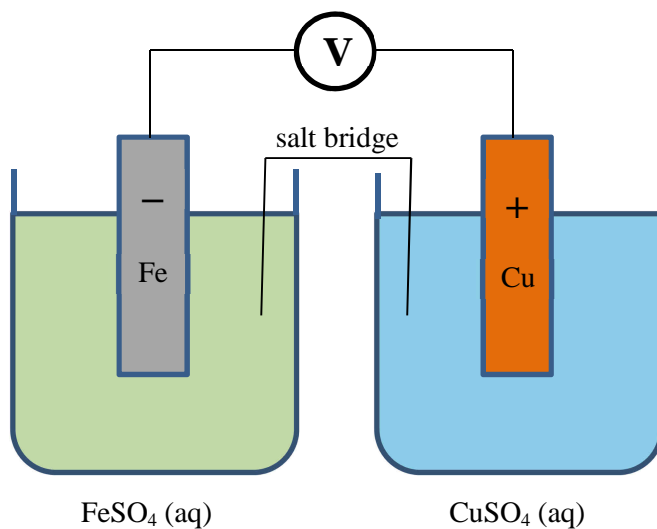
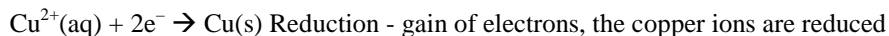
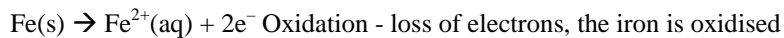


Fig. 17. Circuit diagram for the iron/copper cell

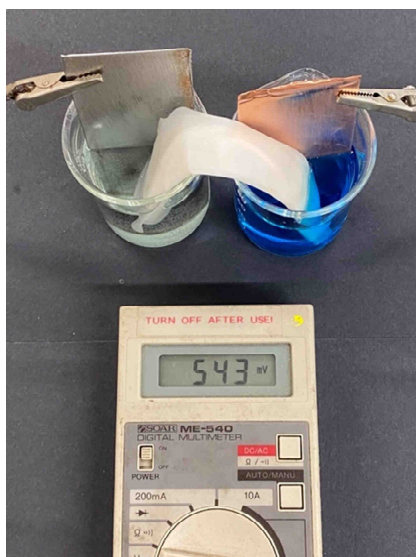


Fig. 18. Part of an electric circuit to show the EMF of an iron/copper cell

It is possible by means of a simple arrangement of apparatus, to show the EMF which is produced in this reaction. This can be illustrated by means of a simple experiment involving two half cells (copper in copper sulphate solution and iron in acidified iron(II) sulphate solution) a salt bridge of potassium nitrate solution, and a voltmeter connected in a circuit. Figure 17 shows a diagrammatic arrangement of the apparatus, and Figure 18 shows the potential difference which is established in such a circuit (the wiring is not shown).

The reading is: $543 \text{ mV} = 0.543 \text{ V}$.

Using standard electrode potentials, the theoretical value of such a cell is calculated as:

$$E^\circ_{\text{cell}} = E^\circ_{\text{RHS}} - E^\circ_{\text{LHS}} = E^\circ_{\text{Cu}} - E^\circ_{\text{Fe}} = 0.344 \text{ V} - (-0.440 \text{ V}) = +0.784 \text{ V}$$

The value of 0.543 V is an acceptable result given that this experiment was not conducted under standard conditions.

Concluding remark

One of the earliest recorded chemical reactions involving metals and metal salt solutions - that between iron (Mars) and copper sulphate (blue vitriol) can serve today as an outstanding example for teaching some important fundamentals of chemistry.

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