born one century earlier. In the very beginning of the 19th century, after the invention of Volta's pile and before the discovery of electromagnetism, several researchers were looking for effects of magnets on chemical reactions. The search was guided by an analogy between electricity (or galvanism) and magnetism. Volta's battery and magnets have opposite poles that exhibited attraction or repulsion. Were there any other equivalent properties? This analogy guided the search for new phenomena. Among other attempts, several researchers tried to produce electrolysis – perhaps the most spectacular chemical effect of Volta's pile – using magnets instead of an electric battery.

This paper will describe the attempts to replace the electrical battery by a magnet during the 19th century. The subject has received no attention from historians of science until now[3]. Since no account of the rise of magnetochemistry has being published hitherto, the aim of this paper will be to provide a detailed description and references on this curious episode.

As shown below, Johann Wilhelm Ritter's early experimental researches on chemical effects of magnets reported positive results, but other researchers could find no effect. For several decades there was a disagreement between experimental reports and it was not altogether clear whether a magnet could produce an electromotive force. In 1834, Antoine César Becquerel supplied a short review of this subject and denied the existence of the phenomenon (BECQUEREL, *Traité expérimental de l'électricité et du magnétisme*, vol. 1, pp. 380-6). In 1843, Leopold Gmelin, in his famous *Handbuch der Chemie*, presented a roll of authors who defended the existence and another list of those who denied the phenomenon, but did not state his own opinion (GMELIN, *Handbuch der Chemie*, vol. 1, p. 514). Towards the end of the 19th century Gustav Wiedemann devoted just a few paragraphs of his treatise on electricity to the description of old works and denied the phenomenon (WIEDEMANN, *Die Lehre von der Elektricität*, vol. 3, § 1125, pp. 967-8). In the same way, Wilhelm Ostwald classified Ritter's work as "galvanic fantasies" (OSTWALD, *Elektrochemie: ihre Geschichte und Lehre*, pp. 216-7).

Most chemists had forgotten this subject towards the end of the 19th century. In the decades of 1880-1890, however, the study of this subject received a new impetus from both the experimental and the theoretical points of view.

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[1] E-mail: rmartins@ifi.unicamp.br

[2] The earliest book on this subject was probably Wedekind's *Magnetochemie*, published in 1911.

[3] No papers on this subject have been found, and books on the history of chemistry, such as Partington's *History of chemistry*, do not mention the search for chemical effects of magnetism in the 19th century. In recent books, such as Meyer's *A history of electricity and magnetism* or *Electrochemistry, past and present* by Stock and Orna, there is also no information about this episode.

However, as the effect was weak and difficult to detect, its practical importance was negligible. The subject was gradually forgotten[4].

RITTER AND THE RISE OF MAGNETOCHEMISTRY

Electricity and magnetism exhibit several well-known similarities. They can act at a distance, and both can produce attraction and repulsion. It was natural to think that there could be a deeper relationship between them, and this led the Bavarian Academy of Science to propose the following prize question (1774-1776): “Is there a true physical analogy between electric force and magnetic force?” The result of the competition was published in Van Swinden’s book, *Analogie de l’éléctricité et du magnétisme*, where one can find descriptions of the magnetic effects of thunderbolts, and very curious experiments, such as G. W. Schilling’s claim that eels are attracted by magnets (VAN SWINDEN, *Analogie de l’éléctricité et du magnétisme*, vol. 1, p. 436). After the discovery of galvanism, attempts were made to new resemblances between magnetism and the new phenomenon. According to Pierre Sue, Fowler observed around 1796 that a magnet could produce muscular contractions, but afterward he noticed that the same effect occurred with a non-magnetic iron bar (SUE, *Histoire du galvanisme*, vol. 1, p. 207). Johann Wilhelm Ritter, however, reported that the contraction effects obtained with a magnet were stronger than with non-magnetic iron[5].

The invention of Volta’s pile, in 1799, led to a renewed interest in the analogy between magnetism and electricity (or galvanism)[6]. Volta’s pile exhibited two opposite poles, thus presenting a strong similarity to magnets. In the following years, this analogy guided the search for several effects. Could a pile work as magnetic needle? Could a magnet produce electrolysis?

Ludwig Achim von Arnim presented in 1800 the earliest known evidence for chemical effects of magnetism. He reported that the North pole of a magnet underwent stronger oxidation in water than the South pole, and an opposite effect in the case of iron attached to a magnet (ARNIN 1800, p. 59). Although he did not attempt to produce a Voltaic effect using

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[4] One can still find a description of this subject in Bhatnagar and Mathur's textbook, *Physical principles and applications of magnetochemistry* (1935), but Pierce Selwood's *Magnetochemistry* (1943) does not describe this phenomenon.

[5] Ritter did not publish any account of his early work on this subject, but it was reported by Humboldt (ARNIN 1800, pp. 60, 63-4).

[6] It was not altogether clear, at first, that galvanism (or the effects of Volta’s pile) was a form of electricity. Ritter was one of the authors who provided several evidences for this identity (see ØERSTED 1803a, ØERSTED 1803b).

Johann Wilhelm Ritter (1776-1810) soon tackled those questions. Hans Christian Ørsted, who was Ritter's friend, reported several of his researches[8]. In one experiment, Ritter had noticed that his so-called "secondary pile"[9] exhibited a very weak electrical effect when it was in a vertical position. The upper end of the pile was observed to become positive, and the lower end negative, and the poles changed when the pile was inverted. He supposed that this effect was due to an external electrical field produced by the Earth, and put the secondary pile in several positions, to find out the direction of the field. When the pile was in a horizontal position, the effect was maximum in the direction North-Northeast to South-Southwest. Ritter concluded that the Earth had electrical poles similar to its magnetic poles, but in different places (ØRSTED 1803a, p. 363). According to him, this showed that the Earth had both a magnetism and an "electricism" (*Electricismus*).

Ritter soon built an electrical compass that was able to point toward the electric poles. He took a thin gold wire and connected its ends through moist conductors to a 200-elements pile[10]. After five minutes the gold wire was put on a pivot similar to those of magnetic compasses, and according to Ritter the gold needle turned to the electric poles of the Earth (ØRSTED 1803a, p. 365)[11].

It is rather curious that in later experiments Ritter built a long (six inches long) bimetallic needle (half its length made of zinc and the other half made of silver) and described that this needle behaved as a magnet, the zinc end pointing to the North and the silver end pointing to the South. Besides that, the needle was also acted by a magnet, in the same way as a magnetic needle (RITTER, *Das electrischen System der Körper*, p. 379).

Ritter's 1803 experiment inspired Jean Nicholas Pierre Hachette and Charles Bernard Desormes to attempt an interesting experiment. In 1805 they built a huge copper-zinc pile with 1,400 metal plates. The length of the pile was about 1 metre. It was put in a horizontal

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[7] In this paper, Arnin stated that when a magnet was kept in water for a night, the South pole became black, while the North pole remained bright.

[8] Dan Christensen presented a very able account of the collaboration between Ørsted and Ritter: CHRISTENSEN 1995.

[9] The secondary pile was built of a series of identical metal disks and wet paper disks. It produced no electricity, but Ritter noticed that it could be charged by Volta's pile, and then it became active for some time (ØRSTED 1803a, p. 347; BERNOULLI, 1805). Ritter's discovery was to lead, much later, to the development of rechargeable batteries.

[10] Ritter had noticed that it was possible to produce an electrical polarity upon metals by this method.

[11] Ørsted declared that he had been unable to repeat this experiment. Ritter published his first claim concerning this effect in RITTER 1803, but he did not provide a description of his experiment. His account was published in 1805: RITTER, *Das electrischen System der Körper*, p. 383-4.

Ritter also attempted to build a "magnetic pile": he used 120 pieces of magnetic iron wire, and connected all those pieces together, with opposite poles of successive pieces attached by a drop of water (ØRSTED 1803c, p. 408). He could obtain no electric effect, however[16].

In December 1805 Ritter presented to the München Academy of sciences a summary of his conclusions:

1. Each magnet of needle may be regarded as equivalent in point of electrical relation to a pair of heterogeneous associated metals. The different poles respectively represent the two dissimilar metals.
2. Consequently each magnet, like these metals, produces electricity. One of the poles gives positive electricity, and the other negative electricity.
3. A circle of magnets also constitutes in analogous circumstances a battery of Volta; and in this manner the author succeeds in demonstrating, by means of the electrometer, the electricities produced by the poles of this circle of magnets.
4. This battery of magnets exercises upon living bodies, or such as are recently dead, on account of its strength, the same effects as a Voltaic column of equal strength.
5. These experiments demonstrate, that in iron magnetized, the south pole yields positive electricity, and the north pole the negative. On the contrary, in the magnetized steel, the north pole yields positive electricity, and the south pole yields negative.

   The same inverse distribution is observed in the oxidabilities (modified by magnetization) of the magnetized body. In iron submitted to this operation, the south pole is the most oxidable, and the north pole is the least. In magnetized steel, it is on

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[12] When a weakly magnetised iron bar of the same weight was put in the same boat, it soon acquired the North-South direction. See also Hachette's later account of his experiment (HACHETTE 1820, p. 165).

[13] The decomposition of water by a voltaic pile was discovered in 1800 by William Nicholson and Anthony Carlisle, but Ritter independently had also discovered the same effect (MOTELAY, *Bibliographical history of electricity and magnetism*, p. 335).

[14] See also ØRSTED 1920, p. 122.

[15] The converse influence of chemical attack upon magnetism had been reported by Tiberius Cavallo, who claimed that after iron was attacked by acids it had a stronger effect upon a magnetic needle (CAVALLO 1786-1787). Afterwards Ruhland reported a similar effect (RUHLAND, 1814).

[16] In 1801, Lüdicke had built a "magnetic battery" with 50 pieces of magnetic wire (LÜDICKE, 1801). He claimed that the North pole produced a stronger effect decomposing water, but later experiments did not confirm his early observations: oxidation seemed sometimes stronger at the North pole, sometimes at the South pole (LÜDICKE, 1802).

Sciences (FRESNEL, 1820, p. 220). However, Fresnel's later experiments did not confirm his earlier findings, and he concluded that the effect did not exist[17]. He also remarked that those experiments led him to doubt Ritter's early results (FRESNEL, 1820, p. 221). One week later, however, Lehot claimed that he had obtained (six years before) regular positive results in investigations similar to those made by Ritter (LEHOT, 1820).

Ten years later, after the discovery of electromagnetic induction, Ampère suggested that Fresnel's experiment could have exhibited the effect of induced currents. Of course, the motion of magnets would produce only short-lived currents, but he thought that the continuous temperature changes of the magnets that must have occurred during those long-term experiments could produce significant currents (BECQUEREL, *Traité expérimentale de l'électricité et du magnétisme*, vol. 1, p. 384).

DIANA'S SILVER TREE

The reduction of metallic salts in aqueous solution produce in special circumstances metallic crystals that build up a treelike (dendritic) structure. This kind of phenomenon had already called the attention of alchemists, who described the so-called "Diana's tree" (*Arbor Dianæ*), build up of silver crystals:

> The Reign of the Moon lasts just three weeks; but before its close, the substance exhibits a great variety of forms; it will become liquid, and again coagulate a hundred times a day; sometimes it will present the appearance of fishes' eyes, and then again of tiny silver trees, with twigs and leaves. Whenever you look at it you will have cause for astonishment, particularly when you see it all divided into beautiful but very minute grains of silver, like the rays of the Sun. This is the White Tincture, glorious to behold, but nothing in respect of what it may become (PHILALETHES, *Secrets reveal'd*, chapter 27, "Of the Regimen of the Moon")[18].

Electricity may quicken the precipitation of those "metallic trees". The "tree of Saturn" can be produced when a copper wire attached to a zinc plate is put inside a diluted solution of

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[17] Yelin repeated Fresnel's experiments and could not observe any positive effect, either (YELIN, 1820, p. 410).

[18] This book of Eirenaeus Philalethes was first published as *Introitus apertus ad occlusum regis palatium* (Amsterdam, 1667) and translated as *Secrets reveal'd: or, an open entrance to the shut-palace of the king* (London, 1669). The complete electronic text of this book can be found in the Internet, in two different versions: at http://clairvision.org/EsotericKnowledge/Alchemy/Hermetic_Museum/Open_Entrance.html and also at http://www.levity.com/alchemy/openentr.html. The citation was taken from the first electronic version.

metallic mercury.

2. A non-metallic steel wire was kept for 14 hours in a solution of silver nitrate and produced no effect; but when the same wire was used to connect the opposite poles of two magnets, “it became speedily plumed with crystals of silver” (MURRAY, 1821, p. 381).

3. A piece of the same wire was cut in two parts. One of them was magnetised and the other was non-magnetic. Both pieces were thrown in the silver nitrate solution. The magnetic wire reduced the silver, the other produced no effect.

4. When a magnet was put inside the solution of silver nitrate, “the North pole became instantly studded with brilliant pallets of silver, and formed more rapidly and more copiously round it than round the South pole” (MURRAY, 1821, p. 381).

Murray’s paper was soon criticised by an anonymous author (B.M., 1882a). “B.M.” repeated all experiments described by Murray. He reported that he observed no sensible difference between magnetic and non-magnetic steel. Murray replied and strongly protested against the anonymous attack: “If *truth* be the object of this writer, why does he blush to own [his name]? Is science to be a masquerade, and its friends appear in false or fictitious characters? An honest man ought to be ashamed of such a contemptible subterfuge [...]” (MURRAY, 1822, p. 121). He conjectured that the steel used by “B.M.” could be slightly magnetic, because the only test that “B.M.” had applied was to check whether it attracted iron filings, and that test was not very sensitive. He also claimed that a magnet could precipitate silver from a solution of silver acetate, and that iron could never produce such an effect. “B.M.” answered to Murray’s reply, but did not comment the two relevant points of Murray’s reply (B.M., 1822b).

Murray’s paper produced some polemical papers in Italy, too. Ridolfi reported that he could not repeat Murray’s results, and recalled that two other physicists (Catullo and Fusinieri) has also disconfirmed those experiments. However, two other researchers, Nobili and Merosi, claimed that they had successfully repeated Murray’s experiments (RIDOLFI, 1822).

The next positive claims came from Norway (MASCHMANN, 1822; HANSTEEN, 1822). A new effect was observed in 1817 by the chemist Maschmann when he was lecturing on Diana’s tree. He put metallic mercury in the lower part of an U-shaped tube, and added a strong solution of silver nitrate. He noticed that the metallic silver “tree” was distinctly brighter and large on one of the sides of the U tube. He noticed that the tube was in the North-

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[19] In the beginning of this paper Murray referred to a former paper “on the decomposition of metallic salts by the magnet” he had presented to the Royal Society of Edinburgh. It seems, however, that this paper was never published.

of strong magnets. Hansteen communicated the results of those experiments to Ørsted in 1819 (HANSTEEN, 1822, p. 241), probably because he knew that the Danish physicist claimed that all natural “forces” were related to one another.

Those experiments were successfully repeated by Johann Schweigger, who was studying a new kind of metallic “vegetation” produced by the reduction of copper solutions: the “Venus tree” or *Arbor Veneris* (SCHWEIGGER, 1825, p. 81). He observed that the metallic tree grew larger towards the North. According to him, Döbereiner also obtained positive results similar to those reported by Maschmann and Hansteen (SCHWEIGGER, 1825, p. 85).

In the same year, Karl Kastner also reported that the reduction of metallic salts was stronger towards the North (KASTNER, 1825, p. 450). Friedrich Dulk, however, could not observe any influence of magnetism on the growth of Diana’s silver tree (DULK, 1825).

THE SITUATION AROUND 1830

It seems that Ørsted’s demonstration that an electric current produces a magnetic effect led many authors to believe that all electric and magnetic phenomena were equivalent. The Abbott Louis Rendu published a paper where he claimed that crystallisation was an electrical phenomenon and called the attention to the similarity between needle-like metallic crystals produced in electrolysis and the arrangement of iron fillings submitted to a magnet (RENDU, 1828a, pp. 310-1). Guided by this analogy, Rendu attempted to produce chemical effects attaching iron wires to the poles of a magnet (RENDU, 1828b). He used a V-shaped glass tube filled with a blue tincture of red cabbage, and introduced the iron wires in each of the branches of the tube. In about 15 minutes the liquid had turned green. It was known that acids would turn this tincture red, and alkalis would turn it green (RENDU, 1828a, p. 314).

Rendu communicated his result to Biot, who conjectured that the effect might be due to a chemical reaction of the iron, instead of a magnetic effect. He suggested to Rendu a new experiment that excluded chemical reaction between iron and water. The iron wires were enclosed in thin glass tubes, closed at its ends, and therefore did not touch the liquid. In the modified experiment the tincture did again become green, as in the former case, but only after 2 hours. Rendu remarked that the tincture turned red, not green, when left to itself (RENDU, 1828b, p. 197).

Rendu’s experiment, communicated to the Paris Academy of Sciences by Biot, called again the attention of researchers to the relation between magnetism and chemical reactions. The journal *Annales de Chimie et de Physique* published Rendu’s account followed by a reprint of Ørsted’s paper on Ritter’s experiments (ØRSTED, 1828) and French translations of Maschmann’s and Hansteen’s papers (MASCHMANN, 1828; HANSTEEN, 1828). Rendu’s iron (WETZLAR, 1829).

After several authors had reported positive findings, the Leipzig physicist Otto Linné Erdmann attempted to ascertain whether those chemical effects of magnetism did really exist (ERDMANN, 1829). He used very strong magnets and repeated every kind of experiment that had been previously described. He noticed that several influences could affect the observed phenomena, and stressed that it was necessary to repeat many times each experiment, in different circumstances(ERDMANN, 1829, p. 34). He noticed, for instance, that the same iron wire, cut into several pieces, exhibited points where oxidation was stronger or weaker, although they seemed exactly alike in all respects. Contact of the wires with the experimenter's hands or with different substances also affected their attack by water and mild acids.

Erdmann tested several reported effects:

1. the influence of terrestrial magnetism on the oxidation of non-magnetic iron wires;
2. the differential oxidation of the poles of magnets and magnetic iron;
3. the influence of the terrestrial magnetic field on the building of Diana's and Saturn's trees;
4. the influence of magnets on the same phenomena;
5. the change of colour of vegetable tinctures by magnetic action.

In a large series of experiments, taking care to avoid spurious influences, Erdmann could observe no positive effect of magnetism in any of those chemical reactions. He concluded that former researchers who had reported positive effects had been mistaken.

Abstracts of Erdmann's paper soon appeared in French (ERDMANN 1829b) and in English (ERDMANN 1830). His experiments seemed convincing and were cited by several authors as a definitive proof that magnetism had no influence on chemical phenomena. In 1831 Jacob Berzelius described Erdmann's researches and remarked that he had also looked for chemical effects of magnetism many years before (in 1812), but obtained only negative results (BERZELIUS, *Jahresbericht über die Fortschritte der physischen Wissenschaften*, vol. 10, pp. 42-3). In his treatise on electricity and magnetism Antoine-César Becquerel described some experiments on chemical effects of magnetism but regarded Erdmann's researches as conclusive against those influences (BECQUEREL, *Traité expérimentale de l'électricité et du magnétisme*, vol. 1, p. 383). Moreover, the 8th edition of the *Encyclopaedia Britannica*, after describing several experiments made by Ritter, Fresnel and Maschmann, presented this final

[20] In the *Annales de Chimie et Physique* and in other journals that quoted the *Annales*, Maschmann's name was mistakenly rendered as Muschman.

[21] A few years later Zantedeschi was to claim that he had discovered electromagnetic induction before Faraday (ZANTEDESCHI, 1834).

meridian (HUNT, 1846b, p. 433). He thought that electricity and magnetism could have some influence in crystallisation and in the lamination of strata, and this led him to start experimental researches on those subjects[22].

In his first communication (HUNT, 1846a) Hunt described a series of experiments that apparently exhibited an influence of magnetism upon the direction of crystallisation. He put a concentrated solution of silver nitrate in two test tubes. One of the test tubes was in contact with a magnet. According to Hunt, crystallisation began first in this tube, growing from the wall close to the magnet (Fig. 1). In the second tube crystals grew slowly and in random positions. Hunt conjectured that perhaps the contact of the magnet with the glass tube wall had just a cooling effect, and made a second experiment: he put a glass vessel containing silver nitrate between a magnet and a brass block. He reported that crystallisation occurred only close to the magnet (Fig. 2).

[Figs. 1 to 7 should appear close to this point]

When one pole of a magnet was put under a glass capsule containing silver nitrate, Hunt observed the formation of regular currents (Fig. 3). Two steel needles attached to the poles of a U-shaped magnet were made to dip in a solution of silver nitrate, and Hunt observed the appearance of curved lines, similar to magnetic lines of force (Fig. 4). Several other experiments reported by Hunt exhibited an apparent influence of magnetism upon the direction of crystallisation of silver nitrate, mercury nitrate and iron sulphate. Besides that, he also reported that the North pole of a magnet produced a stronger effect upon the crystallisation of those substances than the South pole (Fig. 5).

Hunt's second paper (HUNT 1846b) described new experiments that confirmed his previous results. In one of these, he put a U-shaped magnet (Fig. 6) under a copper plate and poured iron sulphate upon it. According to Hunt, there appeared three lines built up of crystal, connecting the two magnetic poles (Fig. 7). Also, more crystals were formed near the North pole than near the South magnetic pole (HUNT, 1846b, pp. 445-6). Finally, Hunt referred to Ritter's experiments and described his own observations that seemed to show that the reduction of metals was stronger close to the North pole. However, when he put iron wires

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[22] In 1822 Maschmann had already suggested that the magnetic field of the Earth could have some influence upon geological structures: "We do not know where those observations will lead us; but I have some reasons to believe that the geologist who follows those researches could in time find out how metals are formed in Nature's workshop" (MASCHMANN, 1822, p. 239). In his second paper (HUNT, 1846b) Hunt referred to the French translation of Maschmann's paper, and it is likely that this paper provided the starting point of his researches.

other researchers, however, had attempted to observe electrolysis using only magnets – without any electric current. As the effect described by Ritter and others was very mild as compared to electrolysis produced by electric current, Wartmann's arrangement was inadequate to exhibit any secondary effect[23].

In another series of experiments, Wartmann investigated the influence of magnetism upon the reduction of copper sulphate by iron. In this case no electric current was applied. He attached soft iron cylinders to the ends of four U-shaped magnets and put the iron cylinders in 8 separate glass vessels containing copper sulphate. The poles of the magnets were put in four different positions, relative to the magnetic field of the Earth. After 15 hours, Wartmann observed and weighed the copper deposits that had formed on the iron cylinders and found them all alike:

> The balance proved that they were all nearly of an equal weight; the slight differences found, which scarcely attained to one- or two-thousandths of the total quantity of copper reduced, are explained by the inequality of development and cleanness of the surfaces of the eight cylinders. The experiment was repeated a great number of times with solutions of copper more or less pure, and more or less concentrated, without the general result varying (WARTMANN, 1847, p. 265)

Wartmann admitted, however, that magnetism had a directing influence upon some chemical actions, and presented some new experiments not unlike those described by Hunt.

It seems that Hunt's confidence in his own experiments was shaken after he read Wartmann's paper. Hunt had already written and submitted to the Royal Society a paper describing "some hundreds of experiments" that had led him to believe that magnetism could have some influence upon the swiftness of chemical reactions, but he withdrew his article (HUNT, 1848, p. 253). After some time, he published a new paper, where he stated that he could not explain the results he had obtained formerly. He maintained that magnetism had a *directing influence* upon molecular phenomena, but claimed that now he had convincing evidence that magnetism *did not* influence the *speed* of chemical reactions.

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[23] Many years later, commenting another similar experiment made by Fossati, Morris Loeb remarked: "I fail to see any significance in the experiment of placing one of two gas-voltameters, or one of two cells containing an iron solution, in a magnetic field, and looking for a difference in the amount of decomposition when a current is passed through the couple in series. Surely no such result could be expected in the face of the universally acknowledged Law of Faraday, unless, indeed, a magnetic field were imagined to alter the quantivalence of the elements" (LOEB, 1891, p. 147).

oscillation, but soon returned to the zero position. The effect was null when one or both iron electrodes were magnetised. Hunt also observed that the electromotive force produced by two different electrodes (one of iron, the other of copper) was not changed when the iron electrode was turned magnetic.

THE REVIVAL OF MAGNETOCHEMISTRY IN THE 1880'S

After the researches of Hunt and Wartmann there was a long period when no new researches were published. Towards the end of the 19th century Gustav Wiedemann devoted just a few paragraphs of his treatise on electricity to the description of old works and denied the phenomenon (WIEDEMANN, *Die Lehre von der Elektricität*, vol. 3, § 1125, pp. 967-8). In the same way, Wilhelm Ostwald classified Ritter's work as "galvanic fantasies" (OSTWALD, *Elektrochemie: ihre Geschichte und Lehre*, pp. 216-7). However, when those books were published, the subject had already attained a new status and well-informed scientists did not doubt any more that magnetism could produce chemical action.

The first paper starting this new period of research was published in June 1881 by Ira Remsen. This author was apparently unaware of previous studies on the influence of a magnetic field in chemical, since he stated: "[...] it should be stated that a careful examination of the literature has failed to show that any experiments of the kind described in this paper have ever been performed" (REMSEN, 1881, p. 162).

Remsen's starting point was the imprecise conjecture that the chemical properties of magnetized metal could be different from that of the same metal unmagnetized. After several attempts he found a positive evidence. He put a vessel of thin, homogeneous iron on the poles of a strong magnet, and poured a solution of copper sulphate over the iron surface. Deposition of copper began at once, and after a few minutes Remsen could observe an outline of the poles of the magnet: "The copper was deposited in a fairly uniform way on the entire plate, except at the lines marking the outlines of the poles. These lines were sharply marked as depressions in the deposit, thus indicating that less action had taken place there" (REMSEN, 1881, p. 159). The experiment was repeated with several different magnets, and the result was always the same. He also noticed that the copper deposit exhibited a series of lines around the poles (Fig. 9). Remsen remarked that the phenomenon always succeeded, with different magnets, and described detailed directions for the reproduction of the experiment.

[Fig. 9 should appear close to this point]

> When iron in the magnetic field is destroyed by acids, a process is performed which may be considered equivalent to its withdrawal by mechanical means to a position of zero potential. Since in such a process energy must be expended, we might expect the heating effect of the reaction to differ within and without the field by an amount equivalent to the energy necessary to withdraw the iron mechanically to an infinite distance (NICHOLS, 1884, p. 134).

According to this argument, Nichols anticipated that the reaction of iron with an acid would release less heat when in the presence of a magnet than otherwise. He made some preliminary experiments measuring the temperature rise when 5 g of iron filings reacted with 100 cm^3 of *aqua regia*. Contrary to expectation, the temperature was much higher when there was a magnet acting upon the iron filings. In a series of 10 measurements using a calorimeter, William Franklin (Nichols' assistant) obtained the release of 1288.8 calories per gram of iron when the magnet was turned on, and only 1035.0 calories per gram of iron when the magnet was turned off – a difference of about 25%.

Remsen reacted to Nichols' paper publishing a short note (REMSEN, 1885) where he called attention to his former work and informed that he was continuing his researches. However, he never published any other paper on this subject[24].

Unaware of Remsen's and Nichols' researches, Theodor Gross began to study the subject using a new approach (GROSS, 1885a; GROSS, 1885b). He was aware that William Thomson had shown that it was possible to produce thermoelectric effects using a pair of magnetic and unmagnetized iron wires. This led him to conjecture that it could be possible to produce an electromotive force using a pair of magnetic and unmagnetized iron electrodes. As shown above, Hunt had already attempted to detect such an effect, obtaining a negative result. Gross, however, reported positive findings. Gross placed two soft iron electrodes in an iron chloride solution. The electric current between the electrodes could be measured by a sensitive galvanometer and there was solenoids were placed around the iron electrodes. When the magnetic field of one electrode was turned on, Gross observed a large and regular deflection of the galvanometer. When the electrodes were perpendicular to one another, the electric current flowed (in the liquid) from the magnetic electrode to the other one. The opposite was observed when the electrodes were parallel to one another. The effect was the same, whether

[24] Ten years later Ira Remsen put his laboratory notebooks at the disposal of F. A. Wolff, remarking that "the results have been disappointing [...] my direct interest in the matter having long since ceased" (WOLFF, 1895, p. 133, footnote by Ira Remsen).

different substances.

It was necessary to obtain some chemical reaction that always led to the same chemical products, both with and without the use of a magnetic field. Nichols described several attempts, including the use of nitric acid, hydrochloric acid and sulphuric acid. He finally chose the reaction of iron filings with hydrochloric acid in the presence of an excess of potassium chlorate because in that case all iron was converted into ferric chlorate, with no trace of ferrous chloride. In that case, he observed that the reaction with the presence of a magnetic field was slower and produced less heating than without the magnetic field (NICHOLS, 1886, pp. 281-2). The experiment was not made in a calorimeter, however, and therefore it was impossible to provide a quantitative comparison between the amounts of heat disengaged in the two cases.

In the reaction between iron and sulphuric acid Nichols thought that the reaction was complete and of the same chemical character both with and without a magnetic field. In this case, he noticed that the magnet increased the speed of reaction and decreased the amount of heat produced. A comparative test measured the speed and heating in a reaction between copper powder and nitric acid. In this case, he observed no effect when a magnet was applied.

Gross continued his researches and published two new papers (GROSS, 1887a, 1887b). He studied the electromotive force between iron electrodes using new electrolytes and obtained positive results with nitric acid. Gross was now aware of Nichols' 1886 paper, which he commented, and attempted to develop a qualitative analysis of the phenomenon using an approach similar to Nichols' – that is, taking into account the variation of the potential energy of iron due to its magnetization and solution (GROSS, 1887a, p. 46). He supposed that the existence of a magnetic potential energy would produce a larger heat of reaction[25]. Afterward, he turned his attention to the electric properties of magnetized iron (GROSS, 1887b) and did not address again the subject of the chemical influence of magnetism.

In 1887 Thomas Andrews also entered the scene, with no acknowledgement of the work of previous researchers (ANDREWS, 1887). He investigated the electrochemical effects of magnetic iron, in a way closely resembling Hunt's and Gross' methods: a magnetic field could be applied to one iron electrode, and he measured the electric current between the two electrodes with a galvanometer (Fig. 10). Andrews reported that in most solutions the magnetized iron electrode became positive relative to the other electrode[26], and that this

[25] It seems that Gross did not remark that the magnetic potential energy of a piece of iron close to a magnet is *negative*.
[26] The opposite was observed, however, when sulphyric acid and hydrochloric acid were used.

1890). Andrews agreed that the magnetic field could decrease or eliminate the initial passivity.

Notice that the interpretation of the observed phenomena was not altogether clear, but now several independent researchers were obtaining positive and strong chemical effects due to magnetism.

THERMODYNAMICS AND MAGNETOCHEMISTRY

Ira Remsen had attempted to explain the reduced deposit of copper at the borders of the magnetic poles as due to a stronger attachment of the iron particles at that place. Colardeau also attempted to explain the phenomenon taking into account molecular causes (COLARDEAU, 1887). He suggested, however, another explanation. He remarked that when copper sulphate is reduced to copper, a corresponding amount of iron is transformed into iron sulphate. This substance will suffer the influence of the magnetic field and would produce, according to Colardeau, an accumulation around the regions of stronger magnetic field, creating a barrier to further chemical attack at those points. This would explain the phenomenon observed by Remsen.

Remsen's and Colardeau's microscopic explanations were naive, as Nichols' and Gross' attempts to account for the observed phenomena using energy considerations were very crude. Thermodynamics was a highly developed theory in those days, and the chemical effects of magnetism soon attracted the attention of theoreticians.

Apparently unaware of Nichols' paper, Paul Janet attempted to prove that the heat disengaged by the dissolution of iron should be smaller when this substance is in a magnetic field (JANET, 1887). Suppose we have a permanent magnet and a piece of soft iron. Janet proposed the following cycle:

1. The piece of iron is first at a large distance from the magnet, and it is brought close to the magnet, with the production of the work τ.
2. The piece of iron is attacked by some substance (for instance, sulphuric acid) and the heat disengaged in the reaction is Q.
3. The iron sulphate is taken to a large distance from the magnet, and the consumed work is much smaller than τ.
4. The iron sulphate is decomposed in such a way that the original iron piece and the sulphuric acid are regained, with the absorption of a heat Q'.

[27] In some circumstances, when iron is immersed in concentrated nitric acid, it does not exhibit any reaction and becomes afterward protected from rusting. According to Andrews, this phenomenon was discovered in 1790 by Keir, who communicated it to the Royal Society (ANDREWS, 1890, p. 117).

change. The thermodynamic potential of a magnetic substance depends on its intensity of magnetization M and temperature T. Taking into account this dependence of the thermodynamic potential, Duhem derived equations that exhibited a dependence of the disengaged heat on the relation between coefficient of magnetization and the temperature (DUHEM, 1888, pp. L.95-L.101). In the case of a magnetic material that is not submitted to an external field (for instance, a permanent magnet dissolved in acid), Duhem concluded:

> If the body entering the reaction is magnetic and if its magnetization coefficient grows or remains constant when the temperature increases, the heat disengaged during the reaction will be larger when the body is magnetized than when it is not. In other cases, it is impossible to predict the sign of the difference between those quantities of heat, *a priori*, without numerical data (DUHEM, 1888, p. L.99).

In the case of a magnetic body submitted to an external magnetic field (for instance, a piece of iron dissolved in acid close to a permanent magnet), Duhem concluded:

> If a magnetic substance enters a reaction and produces a chemical product that has a negligible magnetism, it disengages a smaller amount of heat when the combination occurs in a magnetic field than when the combination occurs outside the field, if the magnetization coefficient decreases or remains constant when temperature increases; if the coefficient increases with temperature, it is impossible to predict anything without numerical data. The same occurs for diamagnetic bodies (DUHEM, 1888, p. L.101).

Duhem also remarked that the possibility of a chemical reaction does not depend on the sign of the heat disengaged by this reaction, but on the change of its total thermodynamic potential W + U – TS, where W is the potential energy due to external forces, U is the internal energy, T is the temperature and S the entropy. Duhem derived that the dissolution of a magnetic body in the presence of a magnetic field entailed a smaller decrease of the thermodynamic potential than in the absence of the magnetic field – and the opposite would hold for a diamagnetic body (DUHEM, 1888, p. L.104). Therefore, in magnetic fields, the chemical reaction would be weaker. If the magnetic field was strong enough, the body would be unable to react.

Duhem's theory did not agree with Janet's simple analysis and the later soon criticized Duhem's paper (JANET, 1889). He pointed out a minor mistake in Duhem's derivations and showed that their analysis agreed as far as the heat developed in iron by its motion in a attained 0.039 volts with a magnetic field of about 10,000 H (NICHOLS & FRANKLIN, 1888, pp. 293-4). The effects obtained in those experiments were regular, and they were able to study the dependence of the electromotive force on the applied magnetic field. In other cases the effect was also significant, but there occurred fluctuations that prevented quantitative study. They also noticed that the products of the chemical reaction that remained close to the electrodes produced a marked influence.

Covering the iron electrode with an isolating wax coating they noticed that the electromotive force depended on the part of the iron piece that was in contact with the solution. If the active surface lay close to the end of the electrode (near the induced magnetic pole), the magnetic electrode would become positive (as zinc) relative to the non-magnetic iron electrode. If the active surface lay in the middle of the electrode (far from the induced magnetic pole), the magnetic electrode would become negative (as platinum) relative to the other iron electrode (NICHOLS & FRANKLIN, 1888, pp. 294-5).

Rowland and Bell also studied the electromotive force of magnetic iron, but arrived to results in opposition to those of Nichols and Franklin (ROWLAND & BELL, 1888). They claimed that the parts of an iron electrode where the magnetic field had a larger *variation* – such as a pointed end – would undergo a weaker chemical attack (as platinum) and would behave as a negative pole (ROWLAND & BELL, 1888, p. 114)[28]. They also challenged the thermodynamic explanation of the effect, and claimed that the potential energy associated to the iron piece in a magnetic field was too small to account for the observed effects.

Andrews published a new series of observations, varying the solutions and keeping a detailed record of electromotive force as a function of time (ANDREWS, 1888). He also noticed that different parts of the magnetic iron electrode acted in different ways, and obtained results similar to those reported by Nichols and Franklin: the ends of the iron rods became electropositive as compared to the middle of the rods.

In all investigations concerning the electromotive force of magnetic iron, no difference had been observed when the magnetic pole of the electrode was changed from South to North condition. Andrews, however, noticed some slight differences (ANDREWS, 1889). Preliminary experiments seemed to show that the North pole electrode became electropositive relative to the South pole electrode. Andrew thought that this result “appeared somewhat singular” and consulted George Stokes before publishing any result. Stokes suggested that the magnetic field of the Earth might be the cause of the observed difference: as the electrodes

[28] The method used by Rowland & Bell was different from that of Nichols & Franklin. The later measured the electromotive force after the galvanometer attained a steady position – and that occurred only some time after the magnetic field was turned on. Rowland & Bell measured the effect immediately after the magnetic field was turned on.

used iron or steel electrodes[29]. Giovan Grimaldi was the first researcher who was able to study a similar effect using bismuth electrodes (GRIMALDI, 1889). That was a significant contribution, because bismuth is a diamagnetic metal and hence its properties are widely different from those of iron. Grimaldi attempted to obtain an electromotive force using bismuth electrodes in a solution of bismuth chloride. His first attempts led to negative results, but after increasing the magnetic field he was able to observe a positive effect. The electric current in the liquid went from the non magnetic bismuth electrode to the other one (GRIMALDI, 1889, p. 167). The effect was highly variable, at first. Grimaldi improved the method of polishing and cleaning the electrodes, and then obtained regular effects.

Grimaldi remarked that the observed phenomenon could not be explained according to the available theories. According to Rowland's interpretation, bismuth should be more easily attacked when it was magnetized, and hence the electric current should have the opposite sense. According to Nichols' interpretation, no effect should be observed, since the potential energy would be negligible in the case of bismuth.

Grimaldi attempted to analyze the phenomenon in a simple way (GRIMALDI, 1889, p. 193). Let B_1 stand for the first bismuth electrode and B_2 the other bismuth electrode. Let L stand for the liquid. The electromotive force ε before application of the magnetic field must be equal to the algebraic sum of the three potential differences[30]:

$$\varepsilon = B_1 \mid L + L \mid B_2 + B_2 \mid B_1$$

where $B_1 \mid L$ stands for the potential difference between the first electrode and the liquid, etc.

When the magnetic field is applied to the first electrode, the electromotive force assumes a new value ε'. The potential difference between the second electrode and the liquid cannot change, and therefore the variation of the electromotive force can only be due to changes of the other potential differences:

$$\varepsilon' - \varepsilon = \Delta(B_1 \mid L) + \Delta(B_2 \mid B_1)$$

If the electromotive force were entirely due to the difference between the two electrodes, that is, if $\Delta(B_1 \mid L) = 0$, the observed effect would be independent of the liquid. That is not the case. Therefore, $\Delta(B_1 \mid L) \neq 0$.

Could the potential difference between the two electrodes be null? Grimaldi also argued that it could not. Indeed, it is possible to obtain a thermoelectric current with two wires of the same metal (in particular, bismuth) when their junctions are kept at two different temperatures

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[29] Nichols attempted to use cobalt and nickel electrodes, but the observed effects were very small.

[30] Of course, the two bismuth electrodes are not in direct contact, but Grimaldi probably assumed that the intermediate conductor (the wire connecting the two electrodes to the galvanometer, and the wire inside the galvanometer) produced no net effect.

It was necessary to study chemical reactions where there was a marked change of the magnetic properties of the substances during the transformation. He chose reactions involving transformation from ferrous to ferric salts, because in those cases the molecular magnetization undergoes a change of about 25%. Two suitable reactions were investigated:

$$6FeSO_4 + KClO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + KCl + 3H_20$$

$$2HI + 2FeCl_3 = I_2 + 2FeCl_2 +2HCl$$

Loeb measured the speed of those reactions both in the presence and without a strong magnetic field. His results were negative: he could observe no influence of magnetism in the speed of those reactions.

Most experiments, however, continued to yield positive results. Thomas Andrews studied the corrosion of magnetic and non-magnetic iron bars in cupric chloride. He observed that the magnetized bars always lost more iron than non-magnetic bars. The difference varied from 0.2% to 9.4%, with a mean of 3.05% in 29 experiments (ANDREWS, 1892). Andrews explained the phenomenon as due to electric currents between the poles and the central parts of the magnetic rods.

George Squier, working under Rowland's supervision, attempted to elucidate the contradiction that had been observed between experiments where magnetism had *prevented* corrosion (Remsen, Rowland) and experiments where magnetism had *accelerated* corrosion (Nichols, Andrews, Gross). Squier made a careful study of the electromotive force in the presence of magnetic fields, using gelatine to control the chemical reactions around the iron electrodes and observing the effects both immediately after the magnetic field was applied and after long times, reaching a few hours (SQUIER, 1893). He observed that the initial effect of magnetization was a *protection* of the iron electrode, that became electronegative. This effect was usually small and difficult to observe when an acid solution was used, because hydrogen bubbles forming on the electrode interfered with the measurement. Adding hydrogen peroxide to the solution, he was able to eliminate the bubbles, and noticed the same initial protective effect as in other reactions. After some time, the effect changed, as the products of the reaction collected around the more strongly magnetized parts of the electrode, and this produced a change in the character of the chemical reaction: ferrous compounds would form instead of ferric compounds, and this would invert the electromotive force – the magnetic electrode became positive. Squier's results seemed to provide an explanation of the contradictions that had been observed by former researchers.

The early experiments by Ira Remsen on the attack of iron plates and deposition of copper in a magnetic field had never received a careful duplication. Although most authors cited Remsen's work, his qualitative method had been replaced by measurements of electromotive force or other quantitative methods. In 1893 Squier and Wolff repeated Remsen's electrodes and took every care to assure that the apparatus was always free from air and from contamination. Instead of the galvanometer, Hurmuzescu used an equilibrium method for measuring the electromotive force, in such a way that the electric current through the electrolyte was null. A very sensitive electrometer (a capillary electrometer invented by Lippmann) was used to establish the equilibrium.

> The use of the electrometer permits the use of a liquid with a very small acid content. In this way the attack of the electrodes is very slow and consequently much more regular, and errors arising from the polarization of the electrodes and from variation of the resistance due to the orientation of the magnetic salts produced by the chemical action, in the magnetic field, are suppressed. On the other side, electrodes with a large surface introduce other causes of error, as a consequence of the lack of homogeneity of solid bodies and because of the particular currents born between differently magnetized parts of the electrode (HURMUZESCU, 1895, p. 119).

The electrodes were thin iron wires (less than 1 mm diameter) enclosed in glass, with flat polished ends. Only those surfaces were in contact with the liquid. He used very weak acids (acetic or oxalic acid diluted in air-free distilled water). One of the electrodes was placed between the poles of an electromagnet, and it was possible to measure the strength of the magnetic field using a coil connected to a ballistic galvanometer[33]. The free surface of the electrode could have two directions relative to the magnetic field: perpendicular or parallel.

The electromotive force generated by the pair of electrodes was compensated using a Daniell cell that provided a very constant electromotive force, and the capillary electrometer that was able to detect 0.0001 volt.

Hurmuzescu used very weak acid solutions with air-free distilled water and took every care to avoid chemical contamination of the apparatus. In those conditions, the system provided repetitive measurements over several days. No former researcher had obtained such unchanging conditions. When he applied a magnetic field to the electrode, he noticed that the electromotive force increased to a maximum and then kept a constant value (sometimes with a very small decrease of a few 10^{-4} V).

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[31] The results presented in this paper were first presented by Wolff in his PhD thesis, in June 1893.
[32] Dragomir Hurmuzescu (1865-1954) was a student of Gabriel Lippmann and obtained his PhD in Paris, in 1896. Afterward he returned to his country, where he was professor of the University of Jassy from 1897 to 1913. From this year to 1937 he was professor of the University of Bukarest.
[33] Only the field produced by the electromagnet was measured. The field on the electrode could be slightly different.

Hurmuzescu also provided the thermodynamic theory of the phenomenon. Suppose that an electric charge *dq* passes from the non-magnetic electrode *b* to the magnetized electrode *a*. At *b* an amount dm_b of the mass of the first electrode will be dissolved in the liquid, and the electrolyte close to this electrode will have a corresponding increase. At *a* the opposite process will occur. At each of the electrodes there will occur a change in their magnetic energy, and at the liquid close to each electrode there will also occur changes in the magnetic energy.

For each active substance in the electric cell Hurmuzescu used the following symbols:

I = magnetization intensity

l = electrochemical equivalent = *dm/dq*

v = volume

δ = density = *dm/dv*

k = magnetic susceptibility[35]

The density of magnetic energy in a substance is proportional to the square of the intensity of magnetization of the substance ($I^2/2k$). Therefore, the change of energy in each active substance of the cell will be given by $(I^2/2k).dv$. Now, the volume added or subtracted from each substance will be

$$dv = dm/\delta = l.dq/\delta$$

Hence, the energy change of each active substance will be

$$(I^2/2k).dv = (I^2/2k).l.dq/\delta$$

If we add the magnetic energy changes of every active substance, we obtain the total energy change corresponding to the transportation of the charge *dq* from electrode *b* to electrode *a*. This energy must be related to the electric energy *E.dq* generated by the electromotive force E. Supposing that there no other forms of energy must be taken into account[36], the electromotive force will be:

$$E = \sum (I^2/2k).l/\delta$$

In Hurmuzescu's experiments there was no magnetic field at electrode *b*, therefore it was only necessary to take into account the terms corresponding to the electrode *a* and the liquid close to it. Besides that, in the case when the magnetic field is parallel to the free surface of

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[34] In this case, the divergence of the magnetic field close to the surface of the electrode was expected to be very small or null, and the magnetic field should produce no attraction of magnetic salts toward the free surface of the electrode.

[35] This quantity is not constant: it depends on the magnetic field applied to the metal. However, for weak magnetic fields it may be regarded as a constant.

[36] Hurmuzescu knew that magnetization changes the volume of magnetic solids and liquids. Hence, there is a mechanical work related to magnetization. In a later paper (HURMUZESCU, 1897-98) he measured this effect and developed a more complete theoretical analysis of the phenomenon.

the body of the electrode; (2) the magnetization of the liquid cannot be neglected, if there are iron salts dissolved in it. Now, the electromotive force will be:

$$E = I^2 l/2k\delta - I'^2 l'/2k'\delta'$$

where the primed symbols refer to the liquid surrounding the electrode. In this case, the electromotive force may be negative, because the first term may be small and the second term may be significant.

Hurmuzescu published a more detailed paper some years later, where he also presented several experimental tables (HURMUZESCU, 1897-1898, part III), but there is nothing essentially new in that article. His findings were soon confirmed by other researchers (LALA & FOURNIER, 1896; PAILLOT, 1900). Hurmuzescu's work was regarded so weighty that he was honored with an invitation to report his researches at the 1900 *Congrès International de Physique*, in Paris (HURMUZESCU, 1900).

René Paillot was one of the few researchers that took the full advantage of Hurmuzescu's work. Working in Lille, he developed a PhD thesis on the electromotive force of magnetization (PAILLOT, 1902), using the same method. It is relevant to remark that Paillot was not working at the same laboratory as Hurmuzescu (who worked at the Sorbonne), nor was he working under the supervision of Lippmann, but he was able to reproduce *all effects* described by Hurmuzescu[37]. In his paper, Paillot emphasised the experimental conditions necessary for the reproduction of the phenomenon and remarked:

> Mr. Hurmuzescu, in a remarkable work, accurately described the experimental conditions that should be chosen to avoid as much as possible the causes of error and to obtain agreeable results (PAILLOT, 1902, p. 209).

Hurmuzescu's experimental method exhibited an exceptional stability. Paillot made two series of measurements with the same system, with an interval of 90 hours, and obtained complete agreement within the experimental error of 10^{-4} V (PAILLOT, 1902, p. 217). Besides confirming Hurmuzescu's results, Paillot also used the same method to study the effect under higher magnetic fields and with varying temperatures. He observed that for very high magnetic fields the electromotive force due to magnetisation inclines towards a limit, and that the effect increases as the temperature of the electrode rises.

Paillot's work confirmed the existence of the curious phenomenon we could name "Hurmuzescu effect". The observed electromotive force due to magnetisation was very small,

[37] It is well known that sometimes an effect can only be reproduced in one single laboratory, by people who obtained their training under the same supervisor.

could predict such effects. During this period, effects reported by several researchers could not be reproduced, and it was not altogether clear whether magnetism did really affect chemical reactions or not. Remsen's work provided a new impetus to the field because it exhibited a simple experiment that could be repeated and yielded reproducible effects. However, the theory of this phenomenon was not entirely clear, and it was only qualitative.

For the first time, after a century of attempts, Hurmuzescu's work was able to isolate and stabilize one special kind of phenomenon: the generation of an electromotive force due to magnetization. Now it became clear that it was possible, indeed, to produce electrolysis using a magnet to create an electromotive force, and the exact conditions for the reproduction of the effect were established.

According to Ian Hacking's terminology, we could say that Hurmuzescu *created* the phenomenon he studied (HACKING, *Representing and intervening*, p. 225). The effect studied by Hurmuzescu occurred in highly artificial conditions that can be found only in the laboratory: it required very small polished electrodes, distilled air-free water, an electric arrangement that avoided electric currents in the cell, etc. Only in those circumstances it became possible to obtain a regular, repeatable phenomenon.

> To experiment is to create, produce, refine and stabilize phenomena. If phenomena were plentiful in nature, summer blackberries there just for the picking, it would be remarkable if experiments didn't work. But phenomena are hard to produce in any stable way. That is why I spoke of creating and not merely discovering phenomena. That is a long hard task (HACKING, Ian. *Representing and intervening*, p. 230)

Hurmuzescu's work represented the end of a long search. This case study presents an illustration of the difficulties in the way toward the establishment of a new scientific phenomenon.

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[40] This was Duhem's PhD thesis. It was also published in book form: *Théorie nouvelle de l'aimantation par influence fondée sur la thermodynamique*. Paris, Gauthier-Villars, 1888.

[41] This periodical had two different titles. It was also called *Jahrbuch der Chemie und Physik*, from volume 30 onwards (with a new numbering of the volumes). *Journal für Chemie und Physik* **56** corresponded to *Jahrbuch der Chemie und Physik* **26**.

[42] This is a short account of Erdman's paper in the *Bibliothèque Universelle.*

[43] A short abstract of this paper was published as: Sopra una corrente galvanica ottenuta col bismuto in un campo magnetico. Nota preliminare. *Atti della Reale Accademia dei Lincei, Rendiconti* **5** (sem. 1): 28-9, 1889. Reproduced in: *Il Nuovo Cimento* **25**: 191, 1889.

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[44] There is an English translation of this paper: On the electro-magnetic experiments of MM. Oersted and Ampere. By Mr. Hatchett [sic]. *The Philosophical Magazine and Journal* **57**: 40-4, 1821.

[45] Hurmuzescu himself presented a wrong reference for this article (volume 5, p. 119) in a later paper 9HURMUZESCU, 1900, p. 562). The wrong reference was reproduced by several authors.

[46] The same work was also published as: Force electromotrice d'aimantation. *Annales Scientifiques de l'Université de Jassy* **1**: 5-14, 1900-1901.

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[48] A translation was published in Nicholson's *Journal*: Experiments on magnetism; by Mr. Ritter, of Jena. Communicated by Dr. Orsted, of Copenhagen. *A Journal of Natural Philosophy, Chemistry, and the Arts* [2] **8**: 184-6, 1804.

[49] Ørsted's paper was reproduced in the *Journal für Chemie und Physik* **29**: 275-281, 1820. It was reprinted in LARSEN, A. (ed.). *The discovery of electromagnetism made in the year 1820 by H. C. Oersted*. Copenhagen, 1920. This book also contains facsimile reprints of early translations (German, French, English, Italian) of Ørsted's work.

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[50] This paper is an abstract of Paillot's PhD thesis: *Recherches sur les forces électromotrices d'aimantation.* Lille: I. Danel, 1901.
[51] This paper was also published in *American Journal of Science* [3] **36**: 39-47, 1888.
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