André-Marie Ampère. The chemical side

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Figure 1. André-Marie Ampère (1775-1836).

Resumen

El nombre André-Marie Ampère (1775-1836) trae inmediatamente a la memoria los conceptos de corriente eléctrica y magnetismo. Es cierto que éstas fueron, de lejos, las más importantes contribuciones científicas de Ampère, pero él también nos dejó ideas químicas básicas respecto a la composición de la materia, incluyendo un enfoque alternativo al concepto de volúmenes iguales = igual número de partículas. Ampère le dió al flúor su nombre antes de que fuera descubierto y jugó un papel importante en la historia del cloro y del yodo.

Abstract

The name André-Marie Ampère (1775-1836) brings immediately to memory the concepts of electrical current and magnetism. It is true that these were by far the most significant contribution of Ampère, but he also left us with some seminal chemical ideas regarding the composition of matter, including an alternative approach to the concept of equal volumes = equal number of particles. He gave the element fluorine its name before it was discovered and played an important role in the history of chlorine and iodine.

Life and career

There are three important books that describe the life and work of Ampère from completely different points of view. Valsons book (Valson, 1986; 369 pages) is actually a hagiography and not a biography. It is an analysis of Ampère based on his religious feelings and the different stages of his adherence to Catholicism, from the very strong and traditional upbringing while at home as a child and during his first marriage, followed by a distancing after the loss

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of his first wife and a return to the basic roots. De Launays book (De Launay, 1925; 275 pages) describes Ampères life against the changing political background providing very little insight into his scientific contributions. Hofmanns book (Hofmann, 1996; 406 pages) is the most recent and comprehensive; it includes the information given in the other two books and substantial information about Ampères scientific work.

André-Marie Ampère was born in Lyon on January 22, 1775, the second child of Jeanne Desutières-Sarcey and Jean-Jacques Ampère, a prosperous silk merchant. Shortly after his birth the family moved to the nearby village of Poleymieux, where André grew up. Antoinette, his elder sister, was born in 1772 and his younger sister, Josephine, was born in 1785. Josephine would become a close companion and eventually would be his housekeeper in Paris.

His father was greatly influenced by the educational theories of Jean-Jacques Rousseau (1712-1778) and decided not to put his son through the traditional teaching system. Instead, he led the young boy to become an autodidact by exposing him to the extensive library he had at home; he never required him to study anything, just to follow his own tastes. One of the first works Ampère read was George-Louis Leclerc Buffon's (1707-1788) *Histoire Naturelle*, which stimulated his lifelong interest in taxonomy. Probably the most important influence on him was Denis Diderot's (1713-1784) newly completed Encyclopédie, which he read thoroughly committing entire articles to his photographic memory; even thirty years later he could recite many of the articles by memory (Hofmann, 1996).

Ampère became interested in mathematics at the young age of 13 when he began to study first elementary texts and then the works of Leonhard Euler (1707-1783) on advanced algebra, probability theory, and calculus, and Joseph-Louis Lagrange's (1736-1813) book on analytical mechanics. Being isolated from scholars in mathematics, he wrote a memoir on conic sections with the materials that he found in these books and some proofs that he believed were new. It is possible that one of these proofs was the basis of the memoir "Rectification d'Une Arc Quelconque de Cercle Plus Petit que la Demi-Circonference", which he submitted to the *Académie de Lyons*

in 1788. In this memoir he analyzed the geometric construction of a linear magnitude equal in length to an arbitrary chosen arc of a semi-circle.

Ampères early education took place in a deeply religious atmosphere. His mother was very religious and arranged for her son to be thoroughly instructed in the Catholic faith. Much of Ampère's philosophical and scientific thought reflected the mixture of the two conflicting ideologies, the Encyclopédie and Catholicism.

Ampères childhood ended in 1789 with the outbreak of the French Revolution and several tragic events. First, Antoinette, André's elder sister, died at the age of 20 on March 2, 1792. She had been his constant companion and she would always remain an important part of his memories of Poleymieux. The next tragedy related to his father, Jean-Jacques, who was called back to Lyon to serve as *juge de paix*, a post with some important police powers. The provisional Girondin government issued warrants for the arrest of prominent Lyonese Jacobins, including Joseph Chalier (1747-1793), their orator and leader. After the change in government, on July 1792 the Jacobin dominated Convention declared the city of Lyon to be in revolt and its administrators to be traitors whose property was subject to confiscation. On October 9 Lyon fell to the troops of the Republic; in the purge that followed Jean-Jacques Ampère was imprisoned, tried, and guillotined on November 23, 1793. This event left young André in a very emotional state.

In the midst of these traumatic events Ampère met Catherine-Antoinette Carron (always referred to as Julie) who was to become his wife. Julie was somewhat older that Ampère and a member of a bourgeois family of good standing. They were married on August 7, 1799, in a clandestine religious ceremony because the revolutionary government prohibited these ceremonies. The next four years were the happiest of Ampère's life. Their only son, Jean-Jacques, was born on August 12, 1800. Unfortunately the marriage lasted less than four years; on July 13, 1803, Julie died of an ailment diagnosed as an abdominal tumour.

On August 1, 1806, Ampère married again, this time to Jeanne Potot. Unfortunately the marriage degenerated almost immediately when his wife told him that she had no intention of bearing children. He persisted, however, and she became pregnant within about two months. His wife and mother-in-law made his life so unbearable that he was forced to leave the house. While living alone he was notified that on July 6, 1807 his wife had given birth to their daughter, Anne-Joséphine-Albine. After the birth of Albine Ampère realized that his only recourse was divorce, which he received together with the custody of Albine. Albine joined Jean-Jacques in Ampère's household, now presided over by his mother and her aunt.

Ampere's two children were also the source of much anguish. The son, Jean-Jacques, was well trained in languages, literature and sciences, and Ampère initially encouraged him to find a position in the chemical industry, but Jean-Jacques insisted upon a literary career. When he was 20 years old he met and fell under the spell of Madame Récamier, the great beauty of the Napoleonic era. Jean-Jacques followed her to Italy and upon his return to Paris in 1824 he separated almost completely from his father. In 1827 Ampère married his daughter to Gabriel Ride, a former officer of Napoleon's army, a man with powerful inclinations for strong drink, violence, and gambling. Beginning 1830 he was repeatedly placed in several institutions for treatment of alcoholism and gave much grief to Albine and to his father-in-law.

Ampère began his academic and scientific career as a mathematics teacher and tutor in Lyons. On February 18, 1802, he was appointed professor of Physics and Chemistry at the *École Centrale* of Bourg-en-Bresse d'Ain. Although he had no formal education, his reputation as a private tutor was judged to be sufficient preparation. In addition to his teaching for the École Centrale, Ampère also taught geometry and arithmetic for a Bourg secondary school. His appointment to the Lyon Lycée coincided with the closure of the departmental *Écoles Centrales*. The Écoles Centrales were intended to produce French citizens receptive to the Enlightenment attitude that progressive social institutions must be grounded on a materialistic conception of human capacities (Hofmann, 1996).

Ampere's first scientific paper was on the mathematical theory of gambling (Ampère, 1802). It was significant enough to gain him the reputation necessary to be named professor at the Napoleonic lycée in Lyons. In this paper Ampère showed that a gamble who has a finite amount of money but faced either a single opponent with infinite financial resources or a large number of opponents with finite resources, would necessary lose all within a finite amount of time.

Ampère also wrote papers on theoretical mechanics and on the classification of the elements (Ampère, 1816abc). His most extensive mathematical work, written to gain election to the Académie des Sciences, was a treatise on partial differential equations (Ampère, 1815b, 1820).

The significance of his paper on probability gained him in 1804 the appointment of répétiteur of analysis at the *École Polytechnique* in Paris. A répétiteur was essentially a tutor to students who were lectured by the professor of the subject. Ampère taught at the École continuously until 1828, and was promoted to full professor in 1815. In 1808 Ampère was appointed *inspecteur* for the *Université Impériale*, created by Napoleon, and was soon promoted to *inspecteur general*, a post he held until his death. His summer months were occupied by long inspection tours of provincial lycées. He also gave occasional courses at the *Athénée des Arts* and the *École Normale*.

On November 28, 1814, he was elected a member of the class of mathematics in the *Institut Impérial*. In September 1819 he was authorized to offer a course in philosophy at the University of Paris and in 1820 he was named *professeur suppléant* (assistant professor) of astronomy. In 1824 Ampère was elected to the chair of experimental physics at the *Collège de France*. A position at the Collège held clear advantages; there were no examinations to grade, students attended from a desire to study with specific professors who were free to design courses around their own research interests (Hofmann, 1996).

Throughout his life Ampère suffered from a steady deterioration of his health, which increasingly impeded his scientific efforts. He also suffered from economic insecurity for most of his life, and had to take a variety of low-paying jobs, most of which involved teaching mathematics at one level or another. In 1836 Ampère's health failed and he died on June 10, 1836, while on an inspection tour in Marseilles. He is buried in the Montmartre Cemetery in Paris, next to his son Jean-Jacques.

Scientific contribution

Ampère is best known as the founder of the science of electrodynamics so it is fit to give first a short summary of his work on this subject before describing his contributions to the science of chemistry.

In 1820 Christian Oersted (1777-1851) discovered that when a wire carrying an electrical current was put near a compass needle, it caused the needle to deflect. Worsted's results were considered sensa-

tional and discussed all over Europe. Ampère promptly realized that Oersted had not fully understood his experiment because he had not taken into account the influence of terrestrial magnetism. In order to verify his hypothesis he devised an arrangement of free rotating magnets that neutralized the earth's magnetic field in a small region. His first results indicated that the compass needle not always aligned itself at right angles to the current-carrying wire and thus he realized not only that his ideas were correct but also that a compass needle could be used as part of an instrument to detect an electric current. With this instrument, which he named *galvanometer*, he mapped the current throughout a circuit made up of a wire and a voltaic pile. Eventually he came to the conclusion that magnetism was not more than electric current moving in *circles*. Ampère concluded that the fundamental interaction in electrodynamics was the force acting between two current-carrying wires and developed his famous formula for calculating the force acting between two wires as long as one knows the strength of the currents and the geometric arrangements of the wires. He summarized his results in his famous book about the subject (Ampère, 1827).

Ampère's main findings are: (a) Two electric currents attract each other when they move parallel to another in the same direction and they repel each other when they move in parallel but opposite directions; (b) these attractions and repulsions are absolutely different from the attractions and repulsions of static electricity; (c) a magnet is only a collection of electric currents produced by the action of the particles of steel upon one another analogous to that of the elements of a voltaic pile, (d) the only difference between the poles of a magnet is that one is to the left and the other to the right of the electric currents which give the magnetic properties to the steel. From his conclusions Ampère was able to deduce Coulombs law of magnetic action and unify the fields of electricity and magnetism on a basic level.

Not everyone accepted Ampère's theory. His primary opponent was Michael Faraday (1791-1867) who showed that current-carrying helixes were not the same as permanent magnets, and that thus permanent magnetism was not the result of circulating electric currents.

In 1881 the Paris Congress of Electricians decided to name the unit of electric current as the ampere. Initially an ampere was defined electro-

chemically as a current, which would deposit 0.001118 grams of silver per minute within a specified type of voltmeter. This unit was subsequently referred to as the *international ampere.* In 1928 the International Committee on Weights and Measures decided to adopt an absolute system of electrical units. This decision led to the 1948 definition of the ampere as "the current in each of two long parallel place one meter apart in vacuum when the force per unit length acting on each wire is 2×10^{-7} Newton per meter".

The mechanistic relation between heat and light
By 1830 the wave theory of heat was being seriously considered as an alternative to, or modification of, the caloric theory. The first extended discussion of heat was two papers published by Ampère in 1832 and 1835 (Ampère, 1832, 1835). He began his first memoir by stating that "thanks to the findings of Edward Young (1681-1765), François Arago (1785-1853), and Augustin Fresnel (1789-1827), it is well known that light is produced by the vibrations of a fluid distributed all over the space and named *ether.* Radiant heat, that follows the same laws in propagating, can be explained in the same manner. But, when heat is transferred from the hottest part of a body to that that is colder, the propagation laws are very different: instead of a vibrational movement transferred by waves (*ondes*), we have now a movement that propagates gradually, so that the part that is initially hotter (and consequently, the one more agitated when heat is explained by vibrations), although loosing heat by degrees, it conserves more that the parts to which it is transmitting heat. This fact gives place to an objection to heat being transferred by vibratory movements."

Ampère recognized at the outset a major difficulty in using the same theory to explain the transmission of radiant heat through space and the conduction of heat through material bodies. In modern terms, the problem was to reconcile the propagation of heat by waves (second-order differential equation in time) in free space, with its propagation as described by Fourier's heat conduction equation (first-order time derivative) (Ampère, 1832; Wisniak, 2002).

Ampère postulated that the total *vis viva* of the system was conserved, *vis viva* being defined as "the summation of the products of the masses of all its molecules by the squares of their velocities at a given moment, and adding double the integral of the sum of the products of the forces multiplied by the differentials of the spaces described, in the direction of those forces, by each molecule" $\left[\sum mv^2 + 2\int\sum F\cdot dx\right]$. This integral depended only on the relative position of the molecules and was taken in such a manner that it would be zero for the equilibrium position about which vibrations took place. If the atoms vibrated while immersed in a fluid, they would gradually lose *vis viva* to it; if initially one atom was vibrating and the others were at rest, then the fluid would transfer some *vis viva* to these other. However, the total *vis viva* of all the atoms would decrease as waves were propagated through the fluid out of the system, unless we supposed it to be enclosed in a container of vibrators (*diapasons*), which were maintained in a state of vibration at a constant *vis viva.* Then eventually all the vibrators would approach the same *vis viva.*

Ampère rejected firmly a doctrine that had dominated atomic speculation during the preceding half-century: "Now, it is clear that if we admit the phenomena of heat to be produced by vibrations, it is a contradiction to attribute to heat the repulsive force of the atoms requisite to enable them to vibrate" (Ampère, 1832). Ampère tried to overcame this objection by showing to which kind of movement were these phenomena due. His explanation was based on the distinction that he made among particles, molecules, and atoms. He defined as *particule* (particle) an infinitely small part of a body, having its same nature, so that a particle of a solid was a solid, that of a liquid a liquid, and that of a gas had the aeriform state. Particles were constituted of molecules maintained at a distance by attractive and repulsive forces; by the repulsion that established among them the vibratory movement of the intercalated ether; and by the attraction, in direct ratio to their masses and the inverse of the square of their distance. According to Ampère *molecules* were an assembly of atoms maintained at a distance by the attractive and repulsive forces proper of each atom, forces that he accepted were substantially larger than those in the previous category. He called *atom* the material points from where these forces emanated and stated his belief that atoms were absolutely indivisible so that although space could be divided infinitely, matter could not.

Ampère distinguished between molecular vibrations and atomic vibrations. In the first, molecules vibrated in mass when they approached or separated

alternatively one from the other. Molecules either vibrated or they were at rest. Atoms of each molecule were always vibrating while they approached or separated one from the other, but always attached to the same molecules. These latter vibrations constituted what he called atomic vibrations. He attributed to molecular vibrations and to their *spatial* propagation all sound phenomena and to atomic vibrations and their propagation in *ether* all heat and light phenomena (Ampère, 1832; Wisniak, 2002).

Derivation of Mariotte's law
According to Ampère (Ampère, 1815a), in the present state of knowledge, and leaving out of account the forces which produced the phenomena of electricity and magnet, the distance and the relative position of the particles of bodies was determined by three kinds of forces: the pressure that they supported, the repulsion between their particles produced by caloric, and the attractive and repulsive forces pertaining to each of these particles that depended upon their nature and bestowed various qualities upon bodies of different species. Ampère argued that the third of these forces was similar to the one that regulated the motions of celestial bodies; it was the origin of phenomena such as cohesion, refraction, capillarity, polarization, and chemical affinity. It was of much shorter range than the distance between gas particles, a claim he justified by noting that mixing of gases that did not combine chemically did not change the total volume. More than that, mixing of oxygen and hydrogen did not give place to condensation, as would have been expected if molecular attraction was significant. Ampère then adopted as a working principle that "les particules sont dans tous les gaz a une distance suffisante pour que les forces qui leur sont propres n'aient plus aucune influence sur leurs distances mutuelles" (the particles in all gases are at a sufficient distance that the forces which are specific to them no longer have any influence on their mutual distances) (Ampère, 1815a).

If the caloric atmosphere around each gas particle made chemical affinities irrelevant, then equilibrium required simply a neutralization of the repulsive effect of caloric by the force due to the pressure exerted by a restraining barrier. Ampère then analysed the situation in which a gas was confined to a vessel closed by a movable piston and made of a material that did not absorb the gas. The repulsion produced by the caloric between the piston and any

particle of the gas would be independent of the nature of the particle and the piston; it would depend only on the temperature t and the distance z between the particle and the piston and could be expressed as a function $\phi(t, z)$. Calling n the number of particles per unit volume (density), then the number of particles in an infinitesimal volume $dxdydz$ would be $ndxdydz$ and the corresponding pressure exerted on the piston by the gas in this element, $n\phi(t, z)dxdydz$. The total pressure was obtained by double integration over the variables, $n\int\phi(t,z)dz\int ydz$. The second integral was related to the dimensions of the system and thus was constant (H) in relation to the first one. The first integral was simply a function of the temperature, $F(t)$. Hence, regardless of the actual values of F and H, the resulting pressure was proportional to n and thus inversely proportional to the volume) (Ampère, 1815a).

Ampère's approach is interesting in that it represents a microscopic point of view without a kinetic theory of gases; the gas particles are imagined to have fixed positions and pressure may be considered as one surface pressing against another. In modern kinetic theory pressure is interpreted as the number of collisions per unit area and per unit time, nevertheless, the Maxwell-Boltzmann distribution of velocities leads to the expression $PV = Nmc^2/3$ where c^2 represents the average square velocity of all the molecules $(c_2 = \sum c_i^2/N)$, that is, all the molecules have been replaced by another population where each molecule has the same velocity c. Since the term N/V represents the molar density, we have essentially the same expression derived by Ampère.

The theory of chemical combination
Claude-Louis Berthollet (1748-1822) was the most prominent French chemist during Ampère's life; he was a well-respected and well-experienced scientist and did not favor "arbitrary hypotheses" regarding the structure of chemical compounds. Thus when Ampère started to develop his theory of predicting a priori the fixed ratios by which bodies combined with each other he was very cautious of the reaction of the scientific establishment. For this reason he agreed to present his ideas in the form of an abstract, a procedure to which Berthollet agreed tacitly. Consequently, he submitted his "abstract" in the form of a long letter (43 pages) to Berthollet; in the opening statement he wrote that he had almost finished writ-

ing a full memoir on the subject and that for the moment he was presenting its summary (Ampère, 1816d). This full memory was never published.

Ampère started the presentation of his ideas by pointing out that according to Pierre-Simon Laplace (1749-1827), matter was composed of material corpuscles that exerted instant forces of attraction acting along the straight line joining the particles and with strength inversely proportional to the square of the separation distance. This representation implied that the same universal laws that regulated the orbits of the planets were also valid for the constituents of matter, the material molecules. It also required accepting the existence of an immaterial caloric fluid made of corpuscles that mutually repulsed and which were attracted by material bodies. Since light traversed transparent bodies easily the ultimate molecules of bodies had to be separated by distances, which were infinitely *larger* than the dimensions of the molecules. For Ampère this meant that the distance among gaseous particles depended *only* on the temperature and pressure to which they were subjected. In this viewpoint, matter at rest was composed of material corpuscles arranged in such a manner that there was *no movement* in a gas, liquid, or solid. The idea of no movement is critical: The three states of matter were essentially "crystalline", their only difference was the amount of ether that separated the particles. It would have to wait until James Clerk Maxwell (1831-1879) for putting the kinetic theory of gases on a solid theoretical basis.

Lack of movement also meant that for equal volumes, the particles of any gas (simple or compound) were equidistant. Or, as Ampère wrote: "que à des pressions et des températures égales, les particules de tous les gaz soit simples, soit composées, sont placés à la même distance les unes des autre" (at equal pressures and temperatures the particles of all simple or composite gases are located at the same distance one from another) and therefore, that "le nombre des particules est dans cette supposition, proportionnel aux volume des gaz" (in this arrangement the number of particles is proportional to the volume of the gas).[1]

The shape of the molecules did not seem to influence the phenomena they caused, these had

to be explained by the manner in which molecules arranged among themselves to build what Ampère named *particules* (particles). A particle was an assemblage of molecules in a given disposition. In order for the space where the particle was located to be three dimensional, it was necessary that the particle be composed of at least four molecules. Ampère named this space, which was shaped as a polyhedron, "forme representative de la particule" (the representative shape of the particle). Each particle was composed of point-like atoms arranged in space as the vertexes of simple geometric solids, such as a tetrahedron, an octahedron, or a cube. The only possible chemical combinations were those that produced geometric solids having a certain degree of three-dimensional symmetry and regularity. In Ampère's theoretical framework the puzzling arbitrariness of chemical activity could be reduced to mathematical certainty: chemistry could be based in geometry.

According to Ampère, the primitive forms recognized in crystallography were representative of the forms present in the other states (gas and liquid), with the molecules actually located in the apexes of the form. Most elementary particles were represented by tetrahedra; by combining with each other they yielded more complex geometrical shapes, such as a parallelepiped, a hexagonal prism, an octahedron, and a rhomboidal dodecahedron, corresponding to particles containing four, six, eight, twelve, and fourteen molecules, respectively. Ampère utilized the geometric theory of crystals that had been developed by René Just Haüy (1743-1822) to explain the geometry of each shape, to show how molecules united to originate the possible representative particles, and to find that the possible forms were limited to 23. Haüy had already devised the concept of the *molecule integrante* to refer to both the simplest unit of crystal structure and the chemical molecule, the smallest particle that retained the chemical properties of a given substance. But Haüy's ideas did not yield an unequivocal solution to the problem of chemical combinations. His basic molecules had their characteristic geometrical shapes when they were disseminated in the solvent *before* crystallization; they also kept it when they were dissolved in the caloric, in their gaseous state (the three crystalline states of matter). This was consistent with Ampère's basic tenet that the geometric shape of the particle did not change during a change of state: "Je suis parti, pour cela, de la supposition que dans le cas

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[1] Ampère added a footnote to his paper (in page 47) indicating that after he had written his memoir he had known that Avogadro had written a paper expressing this same idea.

où les corps passent à l'état de gaz, leurs particules seules soient séparées et écartées les unes des autres par la force expansive du calorique à des distance beaucoup plus grandes que celles où les forces de affinité et de cohésion ont une action appreciable" (I have started from the supposition that when a body passes to the gaseous state its particles become separated by the force of caloric to a distance much larger than that when the affinity and cohesion forces are important).

Admittance of these hypotheses led to the important consequence that it was enough to know the volume of a composite gas to determine the number particles of each of the primitive gases which were contained in one particle of the composite gas. Here Ampère introduced the second basic assumption, namely, that the common elements hydrogen, oxygen, and nitrogen had particles made up of four molecules. Thus, for example, nitrous gas contained half of its volume of oxygen and half of nitrogen; consequently, one particle of nitrous gas was formed by the reunion of half a particle of oxygen and half a particle of nitrogen. In other words, the particles of nitrous oxide must also be composed of four molecules, two of oxygen and two of nitrogen. In his letter to Berthollet Ampère claimed that according to his theory chlorine particles (molecules in today's terms) had to be composed of *four* molecules. Since this result did not fit the experimental evidence on chlorine, it was necessary to assume that either a chlorine particle was composed of eight molecules (a parallelepiped), or that it contained four molecules of oxygen and four molecules of an unknown combustible body. In the same paper Ampère wrote that Humphry Davy's (1778-1819) recently discovered *euchlorine* (ClO_2) (Davy, H., *Phil Trans.*, 101, 155-162, 1811) had a remarkable volumetric composition. Heating the gas yielded two volumes of hydrogen and four of chlorine, a ratio that was against all the analogies he had drawn. Ampère believed that this unusual composition could only by justified by the assumption that euchlorine was impure and contained a small amount of chlorine. Of the five volumes of the gas used by Davy only four of them were composed of oxygen and chlorine.

The basis of a simple chemical compound was the interpenetration of pairs of particles, one from each element, to generate a common centre of gravity and another regular polyhedron from the total assemblage of the two sets of molecules. Although Ampère did not explicitly say so, he implied that

when *half* of a particle combined with a *full* particle of another element, the total collection of molecules adopted a new configuration corresponding to one of the acceptable structures. Water molecules, for example, were octahedral made up of six molecules of which four came from a hydrogen tetrahedron and two from one half of an oxygen tetrahedron.

We see that the clue to a chemical reaction was found on the possibility of superposition of these geometrical figures: "quand des particules se réunissent en une particule unique, c'est en se plaçant de manière que les centers de gravité des particules composantes, étant au même point, les sommets de l'une se placent dans les intervales qui lasissent les sommets de l'autre et réciproquement. Si les formes representatives resultant de la reunion de plusieurs tétraèdres et plusieurs octaèdres ne sont pas régulières, elles doivent être rejetées" (when the particles unite into one particle, they locate themselves in such a way that their centers of gravity are at the same point; the apexes of one locate themselves between the apexes of the other, and viceversa). Ampère made a thorough geometrical analysis of the manner in which the basic polyhedra could join geometrically in order to generate other acceptable regular polyhedra. For example, for the tetrahedron and the octahedron there were only 23 permissible forms (Ampère coined the names for several of them). He summarized his findings in a table describing each shape, the number of tetrahedra and octahedral that could generate it, the number of apexes, and the total number of faces that the figure had (figure 2). For example, a body A whose particles were shaped as a tetrahedron could combine with a body B having particles shaped as a octahedron only in the ratios A : B = 2:1 (because the union of two tetrahedra and one octahedron yielded a dodecahedron), or A : B = 1:1 (because two octahedra could unite with two tetrahedra to form a cube). Any other ratio would yield an unacceptable geometric shape (Ampère, 1816d).

Ampère felt that the beauty of his theory was a major factor in its favor; furthermore, the theory did have an empirical basis in the sense that his primitive forms were those recognized in crystallography and were indeed regular polyhedra.

Ampère's own attempts to apply his theory were disappointing. Ampère's claim was that his table was the key to possible combinations of elements and the proportions in which they combine. But in practice the table gave little guidance. For example, there are

21 possible combinations of tetrahedra and octahedra up to and including the case of six tetrahedra combined to form a hexa-tetrahedron. Of these 21 possibilities, Ampère's system recognized 14 as feasible chemical compounds. The system was thus not a very efficient mechanism for predicting actual compounds for the simple elements represented by tetrahedra such as oxygen, hydrogen, and nitrogen (Hofmann, 1996). Furthermore, the theory provided little guidance even in relatively simple cases such as water. It also required the user to be quite knowledgeable in space geometry, and to be able to visualize the resulting three-dimensional figures to decide if they were acceptable or not. This was not an easy job at a time when hand models were not available.

As mentioned above, Ampère felt that his method allowed an easy calculation of the molecular weight of all the molecules of simple bodies. In the case of a composite body, it was enough to make an approximate chemical analysis of the same in order to know how many molecules of each component were present. More than that, the method allowed deducing the ratios between acid and basic parts, as well as the amount of water of crystallization present. In addition, Ampère's theory of chemical combination allowed determination of atomic weights, which he named "les poids respectifs des molecules de tous les corps simples". To do so it was enough that the number of molecules obtained corresponded to the polyhedra included in his table.

According to Ampère, the formation of ammonium chloride, a solid compound, resulted from the combination of two gases: Hydrogen chloride, having an octahedral shape, joined with an equal volume of ammonia, which was represented by a cube. The salt particles formed had to have a rhomboidal dodecahedral shape and "cette sel est en effet une de celles qui appartiennent au système de cristallisation du sel ammoniac" (this salt is actually one belonging to the crystallization system of ammonia chloride) (Ampère, 1816d).

As pointed out by Morselli (Morselli, 1984) Ampère's approach was unable to explain the behavior of gaseous combinations of odd ratios of components. Such was the case, for instance, of water and ammonia. According to Ampère, since one volume of water vapor was formed by one volume of hydrogen and half its volume of oxygen, then the vapor particles were composed by one hydrogen particle of hydrogen and half a particle of oxygen. Similarly, one volume of ammonia was formed by the combi-
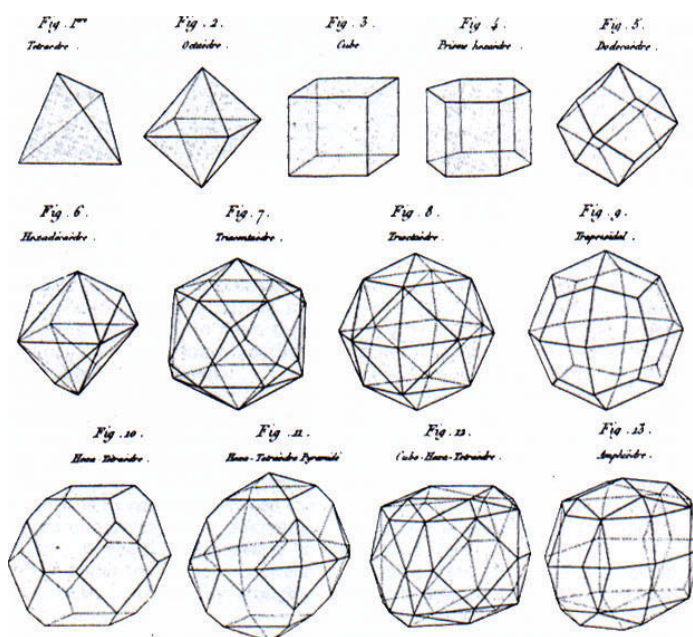

Figure 2. Ampère's geometrical structures of chemical compounds.

nation of half a volume of nitrogen and one and a half volumes of hydrogen; consequently, one particle of ammonia should result from the combination of half a particle of nitrogen and one and a half particles of hydrogen, which of course contradicted Ampère's basic tenets. The answer to this paradox came after Amedeo Avogadro (1776-1856) suggested that the compound molecules, once formed, would undergo a division leading to bi, tri, and tetratomic molecules in agreement with the number of elementary molecules entering into combination.

We have mentioned already Ampère's remark that Avogadro had previously published a similar conclusion (equal volumes = equal number of particles) (Avogadro, 1811, 1814; Wisniak, 2000). Although Avogadro's linked the chemical and physical properties of the elementary particles to their geometrical form, he did not elaborate on the specific geometrical form assumed by the particles. Those of very cohesive elements had "une forme allongée" (elongated shape) with centres where their masses were concentrated. When condensed to form the solid state, the distances between these centres were still too large to allow their masses to influence and attract each other. This meant that very oblong molecules like those of carbon, displayed great cohesion and hardness more as a result of their mutual

position and shape than as effect of gravitational attraction. Molecules reacted by first dividing lengthwise, leaving them more spherical. (Avogadro, 1811, 1814; Boato, 1996).

The discovery of the halogens

Ampère played an active part in the discovery of the three halogens, chlorine, iodine, and fluorine, although he did not perform experimental work on them.

In the beginning of the nineteenth century systematic studies were initiated to analyze chlorine and determine its composition. One classical procedure used at that time was to heat the material in question with carbon in order to find whether it contained oxygen or not. In 1810 Humphry Davy (1778-1819) made a detailed analysis of a paper that Joseph-Louis Gay-Lussac (1778-1850) and Thénard had published on the subject (Gay-Lussac, Thénard, 1809) and commented that it was remarkable that carbon heated white had no action on oxymuriatic acid, a result that made him doubt that this substance contained oxygen (Davy, 1810, 1811). In a following publication he claimed that to call oxymuriatic a gas that did not contain neither muriatic acid nor oxygen, was contrary to the principles of chemical nomenclature. For this reason, and after consulting with several colleagues, he thought it appropriate to give the material a name based on its color, one of its most characteristic properties. Consequently, he suggested calling it *chlorine*, from the χλωροζ, green.

On November 1, 1810, Ampère sent a letter to Davy congratulating him on the discoveries he had made, particularly those related to chlorine and its properties, and that he, Ampère, was struck by the analogy that seemed to exist between oxygen and oxymuriatic acid. The latter formed with combustible substances such as hydrogen, sulfur, phosphorus, and tin, acids that could be named sulfur-muriatic acid (the red liquor of Thomson, S_2Cl_2), phosphoro-muriatic acid (PCl_3), stanno-muriatic acid (*beurre d'etain*, $SnCl_2$), and others. In addition, it seemed to Ampère that the oxygen produced when liquid oxymuriatic acid was exposed to the action of light, originated from the decomposition of water ($Cl_2 + H_2O = 0.5O_2 + 2HCl$). Similarly, black oxide of manganese generated oxymuriatic acid because the oxygen it contained joined with the hydrogen present in hydromuriatic acid ($MnO_2 + 2HCl = Cl_2 + H_2O + MnO$). The two chemical equations as written do not appear, of course, in Ampère's letter, but their

verbal description does so, which Davy did no do (Scheidecker-Chevallier, 1994).

An interesting aspect of the history of fluorine is that André-Marie Ampère (1775-1831) gave it its name before it was isolated. Ampère's interest in chemistry led him to deduce that hydrogen fluoride was analogous to hydrogen chloride. He believed that "silicated fluoric acid" (hydrofluosilicic acid) contained a peculiar principle, analogous to chlorine and oxygen, united to the basis or silica, or *silicum*; the fluoboric acid of the same principle united to boron; and the pure liquid fluoric acid that resulted as this principle united to hydrogen. During the Napoleonic wars with England, Ampère succeeded in sending two letters to Davy (Ampère, 1885) in which he exposed his ideas regarding fluorine. The first letter contained a suggestion that the unknown substance combined with hydrogen in hydrogen fluoride might be separated by electrolysis of the anhydrous acid using a carbon anode: "Reste à savoir si l'éléctricité ne décomposerait pas l'acide hydrofluorique sous sa forme liquide, lorsqu'on en aurait écarté l'eau le plus possible, en portant l'hydrogène d'un côte et oxyfluorique de l'autre" (it is left to be known if electricity will decompose hydrogen fluoride in the liquid state, after most of the water has been eliminated, delivering hydrogen on one side and hydrofluoric acid on the other).

In his second letter Ampère changed the name of the element from oxy-fluorique to *fluore* (fluorine) to harmonize it with the then recently adopted name chlorine. Shortly thereafter, Ampère abandoned the term *le fluore* in favour of *le phtore* (from the Greek *phtoros*, destructive): "J'ai choisi le nom *phtore*, de l'adjectif grec φυοριοζ(on di aussit φυορος, qui se prend dans les deux sens substantif et adjectif), délétère, *qui a la force de ruiner, de détruire, de corrompre*" [I have selected the name *phtore* from the Greek adjective φυοριοζ (also φυορος that is simultaneously a noun and an adjective), meaning to delete, that has the force to ruin, to destroy, to corrupt].

Towards the end of 1811 Bernard Courtois (1777-1838) observed that treating the mother liquor of saltpetre made from varech (algae ashes) with sulfuric acid led to the formation of a crystalline residue that had the remarkable characteristic of generating a violet vapor under the action of heat and having a metallic appearance at room temperature. Courtois wanted to continue his research but he had only limited facilities at his service. Thus towards 1813 he requested from Charles-Bernard Desormes (1777-

1862) and Nicolas Clément-Desormes (1779-1842) to continue his research and communicate his findings to the scientific community. On November 29, 1813 Clément read a memoir to the *Académie des Sciences*, France, in Courtois's name, announcing the discovery of the new element (Clément, 1813) and describing the procedure to prepare it. In his report Clément suggested that the new element combined with hydrogen yielded a material that looked like *acide muriatique.* In the two sessions held on December 6 and December 20 of the same year, Gay-Lussac established the relation between the new body the other elements and named it *iode*, from the Greek ιοειδηζ, violet, because of the color of its vapors (Gay-Lussac, 1813a, 1813b).

At this stage two unfortunate incidents took place. First, Ampère sent another letter to Davy in which he wrote that the existence of the two comburents, oxygen and chlorine, had been proven beyond doubt, and that they would soon be joined by fluorine, and perhaps also by a fourth new substance, recently discovered in France, about which he could not yet provide Davy with details. Now, when Davy visited France on October 1813, he was met by Ampère, Clément, and Desormes, who provided him with a sample of the new substance discovered by Courtois. Davy made a rapid study of it and promptly sent a letter to Georges Cuvier (1769-1832), the permanent secretary of the *Académie*, communicating his findings.

In this letter, read at the Institute on December 13, 1813, five days after the reading of Gay-Lussac's first note, Davy reported his experimental results on the combination of the new material with sodium, potassium, metals, and certain gases and confirming some of Gay-Lussac's results. Davy stated he had come to the conclusion that iodine was a simple body and that the acid obtained by the action of phosphorus on it was a hydrogenated compound; he also realized that he had in his hands a new element.

The haste shown by Davy in publishing his first results, after the first communications to the Académie, and the insinuation of British journals that tended to give to Davy the priority of the discovery, irritated Gay-Lussac to such an extent that he saw it proper to reestablish the facts in his extensive memoir about iodine, published in August of the following year (Gay-Lussac, 1814). All these incidents put Ampère in a delicate situation with his French colleagues, particularly by his having provided a sample to Davy, the citizen of a country that was at war with

Figure 3. Ampère´s name on the Eiffel Tower.

France. In a letter to one of his friends (De Launay, 1936, vol. 2, 458-459) Ampère complained bitterly about the criticism: "That one of the members whose friendship ought to be the most assured, has reproached me, to the point of the gravest insults, about my correspondence with Mr. Davy as a crime."

Epilogue

As a suitable epilogue we can remark that when Gustave Eiffel built his famous tower in 1889, he decided to honor 72 distinguished French scientists by putting their names in the structure. This "invocation of science", as Eiffel called it, reflected his worry over accusations that the tower was useless and waste-less.

There are eighteen names per side of the tower, all positioned just below the first platform of the structure, on the outside. The letters in the names are 60 cm high. Ampère's name is located on the first facade, opposite the Trocadero (Figure 3). It befits that his name is located next to that of Laplace, who so strongly influenced Ampère's view of the physical world.

References

Ampère, A. M., *Considerations sur la Théorie Mathématique du Jeu*, Frères Perisse, Paris, 1802.

Ampère, A. M., Démonstration de la Rélation Découverte Par Mariotte, Entre les Volumes des Gaz et les Pressions qu'ils Suporttent à une Même Température, *Ann. Chim.*, **94**, 145-160, 1815a.

Ampère, A. M., Considérations Générales sur les Intégrales des Équations aux Différentielles Partiales, *J. École Royale Polytechnique* **10** (cahier 17, January), 549-611, 1815b.

Ampère, A. M., Essai: D'une Classification Naturelle Pour les Corps Simples, Part II, *Ann. Chim. Phys.*, **1**, 295-308, 373-394, 1816a.

Ampère, A. M., D'une Classification Naturelle Pour les Corps Simples, *Ann. Chim. Phys.*, **2**, 5-32, 1816b.

Ampère, A. M., D'une Classification Naturelle Pour les Corps Simples, Part II, *Ann. Chim. Phys.*, **2**, 105-125, 1816c.

Ampère, A. M., Lettre de M. Ampère à M. le Comte Berthollet, Sur la Détermination des Proportions Dans Lesquelles les Corps se Combinent d'Après le Nombre et la Disposition Respective des Molècules Don't Leurs Particules Intégrantes Sont Composées, *Ann. Chim.*, **90**, 43-86, 1816d.

Ampère, A. M., Mémoire Contenant l'Application de la Théorie Exposée Dans le XVIIᵉ Cahier du Journal de l'École Polytechnique, à la Intégration des Équations aux Différentielles Partielles du Premier et du Second Ordre, *J. École Royale Polytechnique*, **11** (Cahier 18, January), 1-188, 1820.

Ampère, A. M., *Mémoire Sur la Théorie Mathématique des Phénomènes Électrodynamiques, Uniquement Déduite de l'Expérience*, Paris, 1827.

Ampère, A. M., Idées de Mr. Ampère Sur la Chaleur st Sur la Lumiére, *Bibliothèque, Universelle des Sciences, Belles-lettres et Arts, (Genéve)*, **49**, 225-235, 1832.

Ampère, A. M., Note de M. Ampère sur le Chaleur et sur la Lumiére Considerées Comme Résultant de Mouvements Vibratoires, *Ann. Chim.*, **58**, 432-444, 1835.

Ampère, Lettres d'Ampère a Davy Sur le Fluor, Printed in *Ann. Chim. Phys.*, **4**, 5-13, 1885.

Avogadro, A, Mémoire Sur les Masses Relatives des Molécules Élémentaires des Corps Simples, ou Densités Présumées de Leur Gaz, et Sur la Constitution de Quelques-uns de leurs Composées, *Journal de Physique, de Chimie et d'Histoire Naturelle,* **73**, 58-76, 1811.

Avogadro, A., Mémoire Sur les Masses Relatives des Molécules Élémentaires des Corps Simples, ou Densités Présumées de Leur Gaz, et Sur la Constitution de Quelques-uns de leurs Composées,

Journal de Physique, de Chimie et d'Histoire Naturelle, **78**, 131-156, 1814.

Boato, G., Atomi, Molecule e Costituzione dei Corpinel Primo Ottocento. I Contributi di Avogadro et di Ampère, *Giornale di Fisica*, **37**, 83-109, 1996.

Clément, N., Découverte d'une Substance Nouvelle dans l'Vareck par M. B. Courtois. *Ann. Chim.*, **88**, 304-310, 1813.

Davy, H., Researches on the Oxymuriatic Acid, its Nature and Combinations; and on the Elements of the Muriatic Acid. With Some Experiments on Sulphur & Phosphorus, Made in the Laboratory of the Royal Institution, *Phil. Trans.*, **100**, Part 2, 231-257, 1810.

Davy, H., On a Combination of Oxymuriatic Acid and Oxygen Gas*, Phil Trans.*, **101**, 155-162, 1811.

De Launay, L., *Le Grand Ampère*, Perrin, Paris, 1925.

De Launay, L., *Correspondance du Grand* Ampère, Perrin, Paris (1936-1943), in three volumes.

Gay-Lussac, J., Sur un Nouvel Acide Formé avec la Substance Découverte par M. Courtois, *Ann. Chim.*, **88**, 311-318, 1813a.

Gay-Lussac, J. Sur la Combinaison de l'Iode Avec l'Oxygène. *Ann. Chim.*, **88**, 319-321, 1813b.

Gay-Lussac, J. L., Mémoire Sur l'Iode, *Ann. Chim.*, **91**, 5-160, 1814.

Gay-Lussac, J. L., Thénard, L. J., De la Nature et des Propiétés de l'Acide Muriatique et de l'Acide Muriatique Oxygéné, *Mem. Phys. Chim. Soc. D'-Arcueil*, **2**, 339-358, 1809.

Hofmann, J., *André-Marie Ampère*, Cambridge University Press, Cambridge, 1996.

Morselli, M., *Amedeo Avogadro, a Scientific Biography,* D. Reidel Publishing Co, Dordrecht, 1984.

Scheidecker-Chevallier, M., A. M. Ampère et la Découverte des Halogènes, *Actualité Chimie*, **101**, 104, 1994.

Valson, C.-A., *La Vie et les Travaux d'André-Marie Ampère*, Vitte et Perrussel, Lyon, 1986.

Wisniak, J., "Amedeo Avogadro- the man, the hypothesis, and the number", *Chem. Educator* [On line], **5**(6), 263-268; S1430-417 (2000).

Wisniak, J., The Heat Radiation Law: From Newton to Stefan, *Indian J. Chem. Technol.*, submitted (2002).