CHEMISTRY IN ITALY DURING LATE 18TH AND 19TH CENTURIES

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- <u>The birth of Electrochemistry</u>

  Luigi Galvani, Alessandro Volta, and

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The birth of Chemistry and Periodic Table

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- 1737

At the Faculty of Medicine of the Bologna University, the first chair of Chemistry is established, and assigned to Jacopo Bartolomeo BECCARI (1692-1766). He studied phosphorescence and the action of light on silver halides

- 1776

In some marshes of the *Lago* Maggiore, near Angera, Alessandro VOLTA (1745-1827), high school teacher of physics in Como, individuates a flammable gas, which he calls *aria infiammabile*. Methane is thus discovered. Two years later, he is assigned, as professor of experimental physics, to the University of Pavia

- 1778

In a letter to Horace Bénédict de Saussure, a Swiss naturalist, VOLTA introduces, beneath that of *electrical capacity,* the fundamental concept of *tensione elettrica (electrical tension),* exactly the name that CITCE recommended for the *difference of potential* in an electrochemical cell.

- 1790-1791

VOLTA anticipates, by about 10 years, the GAY-LUSSAC linear dependency of gas volume on temperature, at constant pressure, and a few years later (1795) anticipates, by about 6 years, the so-called John Dalton's rules (1801) on vapour pressure

- 1790

Luigi GALVANI (1737—1798), a physiologist and anatomist, while applying an electrical stimulus to a sectioned frog, observed, by touching the crural nerves, that convulsive movements occurred along its limbs, and attributed this phenomenon to *animal electricity*, as well as to a connection between *electricity and life*. VOLTA's controversy on this point of view is well known; but finally he recognised the pioneering value of Galvani 's experiments, when his successful studies on the connection between *chemical energy and electricity* lead to the discovery, a few years later (1799-1800), of the *pila di Volta*. Phenomena occurring in this device to convert *chemical energy into electrical energy* have been also named *galvanism* (galvanic cells)

- 1792

Luigi Valentino BRUGNATELLI (1761-1818), professor at the University of Pavia since 1796, edits *Annali di Chimica.* Some years later (starting from 1800), by using the *pila di Volta* (electrochemical cell able to convert chemical energy into electrical energy), he studies the reverse phenomenon (*electrolysis*, that is use of electricity to produce chemicals)

- 1799

VOLTA, coming back from Pavia to Como (because the University of Pavia was suppressed by the Austrian rulers, and bonapartist professors were banished) was studying, around these years, what we now call *VOLTA's effect*.

When putting into contact different metals, due to different energy levels of their conduction bands, an electron flow takes place.

In those times, anyway, this quantum mechanical explanation was far from being reached. Towards the end of 1799, however, VOLTA's distinction between *dry metals*, for which the VOLTA's effect applies, and *humid metals*, when, in the presence of conducting salts or acid solutions, a more remarkable flow of electricity occurred, was made clear. For the first time in the history of physics and chemistry, conversion of what we call chemical energy into electrical energy was clearly shown, by a device, which VOLTA himself called *pila* (alternate and vertical piling up of two metals, put in mutual contact by an ionically conducting solution or medium).

On March 20th, 1800, a communication was sent by VOLTA to Sir Joseph Banks, president of the Royal Society, by which he announced to the scientific community the invention of his *electromotive apparatus,* or *artificial electric organ*, as compared to the natural organs of some fishes. The communication was published on *Philosophical Transactions*, with the title *On the electricity excited by the mere contact of conducting substances of different kinds.*

After the Marengo's defeat of the Austrian Army (June 14th 1800), the first Consul Napoleon Bonaparte reopened the University of Pavia, and reinstated , by a specific decree, Alessandro VOLTA as professor of experimental physics, and director of the physics laboratory.

High esteem and honours attributed by Napoleon to Volta, during the visit paid by VOLTA and BRUGNATELLI, to present VOLTA's discovery at the *Institut de France* (November 7th 1801) are well known, and historically documented. VOLTA was designed as foreign member of the *Institut* and awarded by the gold medal, with a life donation, as well as (in 1805) by the *Légion d'Honneur* award. In 1809 he was designed as senator, and one year later count, of the *Regno d'Italia* , created by Napoleon at his peak.

In 1816, the VOLTA's *Opera Omnia* were published in Florence. In 1819, VOLTA retired to private life, and died in his country house of Camnago (now a fraction of Como, named, in his honour, Camnago Volta) in March 5th 1827, at the age of 82.

In 1822, five years before the death of VOLTA, Amedeo AVOGADRO and Vittorio MICHELOTTI set up in Turin a series of fundamental experiments, to develop the chemical theory of *pila di Volta*, and understanding, in terms of chemical reactions, the conversion of chemical into electrical energy, as well as the reverse process, which BRUGNATELLI had been pioneering in the early 19th century, that is the use of electrical energy, generated by VOLTA's cells, to produce chemicals.

The loop was thus closed, and a new branch of Chemistry, ELECTROCHEMISTRY, was ready to take off, in the name of VOLTA.

An epistemological consideration:

Just one hundred years (1899-1900) after the date of VOLTA's discovery of electrochemical cell, in a period dense of new discoveries, officially on December 14th, 1900, at 5 pm, in the *Institute of Physics* of Berlin University, Max PLANCK presented a lecture, *Zur Theorie des Gesetzes der Energieverteilung in Normalspektrum*, in which PLANCK, for the first time in the history of physics, introduced the *quantum*, a small energy quantity, as a "formal assumption", of which probably not even himself realised, at that time, the tremendous importance.

A revolution was beginning in physics. Only a few years before, PLANCK did not firmly believe in atomic theory, which, on the contrary, had been the base of all the chemistry of the 19th century, and was strengthened by Ludwig BOLTZMANN, in his studies on the second principle of thermodynamics.

PLANCK, effectively, during the two or three years which preceded the turn of the century, disapproved the statistical and probabilistic approach of BOLTZMANN towards the second principle, and was strongly polemical towards the whole atomic theory.

Fortunately, just during the studies on the energy distribution in the spectrum, PLANCK recognised his debt towards BOLTZMANN, proposed to call *Boltzmann's constant* the *k constant* of his equation on energy distribution, which was the same as that of statistical interpretation of the second principle by Botlzmann, and proposed in 1905 and 1906 the Nobel prize for the austrian scientist.

But, unfortunately, it was too late. Boltzmann, feeling isolated and unappreciated, died in Duino, near Trieste, on September 1906, at the age of 62. Boltzmann was wrong in despising himself: he was among the most respected and admired physicists of the 19th century, and Planck, at the end, described his work as "one of the most beautiful triumphs of theoretical research".

In fact, the atomic theory and what we now call the quantum theory were complementary, as shown, since the beginning, by the Kirchhoff's equation on energy distributions, investigated by Wien and afterwards by Planck, giving rise to the revolution of quantum physics and quantum chemistry throughout the 20th century.

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CHEMISTRY AND PERIODIC TABLE (1)

About 40 years **before** the birth of **RADIOCHEMISTRY**, a great debate was taking course in **CHEMISTRY,** concerning the essence itself of this new-born science, from the question of atomic and molecular weights to periodical properties of the elements and their compounds.

But, even about four decades before, **Amedeo Avogadro**, count of Quaregno and Cerreto, basing on the work by **Joseph Gay-Lussac** (1808) had published in the edition of July 14th 1811 on *Journal de Physique, de Chimie et d'Histoire naturelle* his paper *Essai d'une manière de déterminer les masses relatives des molecules élémentaires des corps, et les proportions selon lesquelles elles entrent dans ces combinaisons*.

CHEMISTRY AND PERIODIC TABLE (2)

The Avogadro's hypothesis was founded on the diversity between atoms and molecules, which **John Dalton** himself was confusing, as well as on the possibility that elements could also be present in a molecular form.

Each chemistry student to-day learns and experiments **Avogadro's law**; but the scientific community of the early 19th century did not accept Avogadro's principles, still when, three years later (1814), **André – Marie Ampère**, showed their validity, even if by another experimental method.

CHEMISTRY AND PERIODIC TABLE (3)

This hostility was primarily due to the fact that, by experimenting with inorganic substances, often these latter underwent dissociation, thus causing major discrepancies with respect to previsions of Avogadro's principle. On the contrary, when studies on organic substances, isolated from natural products or synthetised, became more frequent, Avogrado's principle was checked again and found to be fully reliable to calculate molecular weights.

The first to have envisaged the potentiality of Avogadro's principle and its correctness has been a young researcher, **Stanislao Cannizzaro,** born in Palermo (July 13 th 1826), who won the chair of chemistry in 1855, at the University of Genoa.

CHEMISTRY AND PERIODIC TABLE (4)

In this University, he published in 1858 *Sunto di un Corso di Filosofia Chimica*, in which he gave the outmost value to Avogadro's principle, by considering that if two gases, in the same temperature and pressure state, contain the same number of molecules, the ratio of their two volumes gives directly the ratio of their molecular weights (what we now call *formula weights*).

For example, if 1 L of hydrogen (a biatomic gas) at 0°C and 760 mm Hg pressure has the weight of 0.090 g, and 1 L of oxygen (an equally biatomic gas) in the same conditions has the weight of 1.43 g, the oxygen molecule should weigh 1.43 / 0.090 times, that is 15.9 times, that of hydrogen.

CHEMISTRY AND PERIODIC TABLE (5)

In other terms, on a relative scale in which the hydrogen molecule has the value of 2.016, the value of the oxygen molecule is 2.016 x 15.9, that is 32.0. This *Cannizzaro rule* allowed to calculate, very reliably, atomic weights, as the *Avogadro's rule* did for molecular weights.

During the presentation of these principles by Cannizzaro, four years after Avogado's death, at the first International Congress of Chemistry of Karlsrule, in 1860, where also **Dmitrij Ivanovič Mendeléev** and **Julius Lothar Meyer** were present, the latter addressed to Cannizzaro a well known appreciation (*you gave us back our sight*). Cannizzaro himself gave, at that Meeting, the full explanation of the apparent deviations from Avogadro's principle, shown by molecules in a dissociation equilibrium.

CHEMISTRY AND PERIODIC TABLE (6)

Four years after the Karlsruhe Conference, in 1864, Lothar Meyer published the first attempt to correlate properties of 28 elements (*periodic Table*) with the concept of *valence*. Only in 1869, following the possibility offered by the Avogadro's and Cannizzaro's criteria to evaluate correctly atomic masses of the elements, Mendeléev was able to fit in this *Table* all elements known at that time, and to foresee the existence of new elements in the *voids* of this Table (the *eka-elements*). The confirmation, a few months later, by Lothar Meyer of the Mendeléev Table, and its substantial periodicity (some exceptions apart) also as a function of atomic weight, as well as the discovery of some of the eka-elements, have been the first outstanding rationalisation of Chemistry, to the birth of which Avogadro and Cannizzaro had given such an important quantitative contribution.

CHEMISTRY AND PERIODIC TABLE (7)

However, it has been **Rudolf Clausius**, with his kinetic theory of gases (1857), and **Jacobus Henricus van't Hoff**, by applying thermodynamic metods to study solutions (1886), and discovering the formal analogies with Avogadro's and Cannizzaro's criteria, to give final approval to Avogadro's hypothesis and to considering this scientist as a founder of atomic - molecular theory.

During these same years, a new science was rising, **Thermodynamics**, potentially able to give to other sciences powerful hints, as has done, among the first ones, to Chemistry.

Thus, towards the end of the 19^{th} century, Chemistry, and the periodic Table particularly, were conceptually ready to the discovery of Radioactivity and to the birth of Radiochemistry.

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The term of *organic chemistry* was adopted for the first time in 1806 by Joens Jacob BERZELIUS, due to the fact that this branch of chemistry was intended to study compounds extracted from living organisms, vegetals or animals, and/or their metabolites.

Only in 1828, the German chemist Friedrich WOEHLER synthesized urea from inorganic intermediates, and showed that the synthetic molecule had the same properties as that isolated from animal organisms.

In 1861 Auguste KE'KULE' defined organic chemistry as "the study of carbon compounds" (with minor exceptions, such as simple derivatives of carbon oxides).

Even if italian chemists, during the 19th century, were predominantly what we would now name *physical chemists or chemical physicists,*, such as AVOGADRO and VOLTA, with a background formation in physics, as was known at that time, some of them had interests in *organic chemistry,* such as CANNIZZARO, or were mainly devoted to organic chemistry as such.

A brief historical outline, for the most important contributors to organic chemistry as such, will be presented in the following slides.

In 1838, Raffaele PIRIA (1814-1865), while studying chemistry with Dumas in Paris, carries out important researches on salycin and on composition of glucosides. His researches are published on *Comptes Rendus de l'Académie des Sciences,* and *Annales de Chimie et de Physique.*

A few years later (1844-1846), while studying asparaginin and aspartic acid, he sets up the reaction which still carries his name (Piria reaction between aliphatic amines and nitrous acid to yield the corresponding alcohols).

At the University of Pisa, he founded the chemical laboratory, which soon became a reference point for chemistry students in Italy (CANNIZZARO has been PIRIA's student in this University, before PIRIA moved to the University of Turin).

In 1847, Ascanio SOBRERO (1812-1888), at the University of Turin, produces, for the first time, nitroglycerol. His researches will constitute the basis of the further studies on this field by Alfred Nobel.

In 1853, Stanislao CANNIZZARO, who, at that time was teaching chemistry at the National College of Alessandira (near Turin), discovered the dismutation of aldehydes, a reaction, which still carries his name. Two years later, he was appointed professor at the University of Genoa.

In 1864, Hugo SCHIFF (1834-1915), at that time professor of chemistry at the Museum of Physics and Natural Sciences in Florence, discovers the condensation reaction of aldehydes with amines (aromatic amines particularly), yielding products, which are still named SCHIFF bases.

In 1878, Francesco SELMI (1817-1881), professor of chemistry at the University of Bologna, studies the toxicologic importance of some alcaloids, a few years after the foundation of *Gazzetta Chimica italiana* (1871), the official organ of italian chemists

In 1881, Giacomo Luigi CIAMICIAN (1857-1922), at that time associated to the CANNIZZARO's group in Rome, before becoming professor of chemistry, first at the University of Padova (1887) and afterwards at Bologna (1889), begins his fundamental studies on pyrrole chemistry, and transformation of five atoms heteroaromatic rings into six atoms rings, like pyridine.

In 1896, Angelo ANGELI (1864-1931), graduated in 1891 at the University of Bologna in the CIAMICIAN's group, discovers nitro, hydroxylamino acid. In 1915 he will be appointed professor of organic chemistry in Florence. His name is tied to the Angeli reaction for aldehydes detection, and to the Angelo-Rimini reaction between aldehydes and N-hydroxybenzene sulphonamides.

SOME CONCLUDING EPISTEMOLOGICAL CONSIDERATIONS

Not always (on the contrary, rarely), in the history of Science, really innovating or revolutionary ideas are rapidly accepted by the scientific community, or soon become the common heritage.

Moreover, sometimes, even who fosters the innovations is not fully aware of their importance, and cannot be, since developments often go beyond the starting ideas and concepts

Two excellent and leading examples of this assertion have been the atomic theory in the 19th century and the quantum theory in the 20th, both of which, starting from physical theories, had an enormous impact on Chemistry.

When, in 1900, Planck introduced the *quantum* concept, he did not really mean that energy could be considered as discreet bullets, but that its way of exchange into heat was such, without varying its nature, which Planck firmly held as undulatory, and only like so.

It has been only five years later, in 1905, that Albert EINSTEIN explicitly considered the *quantum of light*, as the smallest energy quantity that one could consider.

Only by this way, the *photoelectric effect* could be explained and quantitatively interpreted, and, for the first time, the *Planck h constant* experimentally evaluated.

And it has been only in 1923 that *Louis de Broglie* realised that EINSTEIN's discovery of 1905 (*the dual nature of energy, both corpuscular and wave-like*) could be generalised and extended to all material particles, particularly to electrons.

The paths of Science are not straight and easy.

In the 17th century, the same occurred to the founder of Science in the modern sense, Galileo GALILEI, and later to Isaac NEWTON.

Newton was born in 1642, the same year in which Galilei died. Einstein was born in 1879, the same year in which Maxwell died. Some kind of torch-bearers, in the language of olympic games.

Let’s all be torch-bearers of Science, no matter how difficult and wearisome this task may be.

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In 1927, just 85 years ago, the International Congress of Physics was held in Como, from September 11th to September 20th, to commemorate the hundredth Anniversary of Volta's death.

On September 16th, Bohr presented for the first time, to the scientific audience, the idea of complementarity such as given by Heisenberg's principle of indetermination, linked to the role of measurement in quantum theory, and the probabilistic interpretation given by Born to the Schroedinger wave function, to constitute the foundation for a new conception of quantum mechanics. This fusion of ideas will soon be named *Copenhagen interpretation of quantum theory.*

Among the audience, at the *Istituto Carducci,* where the meeting was held, Born, de Broglie, Compton, Heisenberg, Lorentz, Pauli, Planck, and Sommerfeld were present.

Two physicists were absent at the Como's meeting of September 1927. Schroedinger had moved, only some weeks earlier, to Berlin, where he was called as Planck's successor, and was consequently involved in urgent home-setting. Einstein refused to touch the then fascist Italy. Bohr would have met him only one month later in Brussels at the famous Solvay meeting, the fifth of the series. Their controversy on the Copenhagen interpretation will continue.

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- Let's all be,

humbly but proudly,

torch-bearers of Science,

no matter how difficult and wearisome this task may be.

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