Chemical Pathways: 150 Years of Evolution of Chemistry

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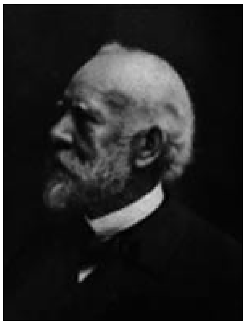
In 1857, a small group of chemists began to meet for informal discussions in Paris, founding the *Société Chimique*. Taking note of its national stature, the society was transformed into the "Société Chimique de France" in 1906. Then, after having merged with the "Société de Chimie Physique", it became the "Société Française de Chimie" in 1984. It celebrates its 150th anniversary this year. The "Société" witnessed the evolution of chemistry and chemists, of their knowledge, and of their goals, as did the other chemical societies created in this era, for example, the Chemical Society of London in 1841, the German Chemical Society in 1867, the Russian Chemical Society in 1868, the American Chemical Society in 1876 or the Chemical Society of Japan in 1878. Can one in a few words seize the impact of these changes?

Marcellin Berthelot



Charles Friedel

In 1857, organic synthesis was still in its infancy. Berthelot achieved the formation of fats by the combination of glycerol with acids in 1854. In addition his syntheses of organic compounds by means of simple chemical methods, such as those used at that time for inorganic derivatives in the famous "electric egg" apparatus, led to the final fall of the theory of a "vital force" inherent in organic compounds. His book *"Chimie Organique Fondée sur la Synthèse"* (1860) had considerable success and presents Berthelot as the founder of this discipline. At the same time, Perkin deposited his patent "Dyeing fabrics" (1856) in England, describing how to obtain dyes starting from residues of the distillation of coal, and this opened the way for the dye industry. After having deposited 152 patents to cover the development of the industrial process, BASF began the production of indigo in 1897. In these crucial years, the structures that allowed the development of the organic chemical industry fell into place: chemical companies (BASF, Hoechst, Bayer, Ciba, Geigy, British Alizarin, les Usines du Rhône, ...), industrial research laboratories associated to academic research, and new developments in chemistry such as chemical engineering, a term that was introduced in England in 1887 by Davis and rose to greater recognition at MIT, expanded rapidly as a required step for industrial scale-up. After having used "simple" reactions like nitration, reduction or oxidation of organic molecules, chemists started to use reactions specific to organic chemistry, for example, preparation of zinc alkyl iodides by Frankland for hydrocarbon synthesis, the Williamson synthesis for the preparation of ethers, and the use of sodium for the condensation of alkyl or aryl halides by Wurtz and then by Fittig. In 1877, Friedel and Crafts used anhydrous aluminum chloride as catalysts for the condensation of aromatic hydrocarbons and alkyl halides. The Friedel−Crafts reaction was applied to the preparation of perfumes, pharmaceutical products, dyes, and then monomers. It is essential to the chemical industry still today, albeit in more eco-compatible forms. A few years later, the Grignard reaction (1900), which allows the formation of a wide variety of organic compounds by the reaction of magnesium with organic iodides, was acquainted with a singular development, unique in the history of chemistry. Another useful tool was the hydrogenation of olefins by using catalysts as studied by Sabatier and Senderens. Progress in organic chemistry was accompanied by the set-up of its nomenclature during the congress of Geneva in April 1892, after two years of work by the Parisian commission of nomenclature chaired by Friedel.

Then a competition started between nature and artifice, between products resulting from nature and those imitating it or exceeding it. To understand the structure of natural products, the chemist decomposed them into small units, and then tried their synthesis. The apotheosis is the total synthesis of vitamin B12, undertaken by Woodward and his team in Harvard, in collaboration with Eschenmoser of Zürich. More than 100 researchers, including Lehn, took part in it. It was completed in eleven years and was announced in Delhi in 1972.

To fight against the shortage of resources and to improve productivity, the chemist found new synthetic routes (e.g. sodium

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carbonate by the Solvay process; ammonia through hydrogenation of nitrogen; hydrocarbons and methanol starting from coal). The list is endless. It widened with the isolation of fluorine by Moissan, the discovery of rare gases by Ramsay, and the disclosure of radio elements by the Curie family.

The chemist also created completely new entities, for example, macromolecules. Polymer chemistry took off in the 1920s with Staudinger, who led the scientific community in the synthesis of long chain polymers, the physicochemical properties of which were intriguing for a long time and began to be explained with the soft matter concepts of de Gennes. The understanding of the organization of soft matter thanks to a large variety of weak interactions between molecules, not atoms, led to the design of numerous new man-made materials with improved performances, or "smart" materials mimicking natural ones. This was further extended to the area of liquid crystals, which are essential components of our everyday life. The design of new synthetic strategies and their industrial achievement allowed the development of alternatives to polymeric natural products like silk (Nylon) and rubber (polychloroprene, polybutadiene, polyisoprene, ...). Moreover, new materials appeared with the design of polyesters and polyolefins starting from C_2-C_6 building blocks obtained from petroleum cuts. Such developments demonstrate again the continuum existing between basic research and industrial processes: the best example is certainly the discovery of the Ziegler–Natta catalysts, which have heavily contributed to the rise of the petrochemical industry.


Marie Curie


Pierre-Gilles de Gennes


Jean Rouxel

The development in the second half of the 19th century of terrestrial (railways, metallic bridges) and maritime communications (and also armament) triggered the progress of metallurgy. Bessemer, Thomas, Siemens, and Martin designed new processes to obtain steels from cast iron; Hall and Héroult patented the electrolysis of alumina and the arc furnace. A scientific vision of industry is also shown by many contributions from Le Châtelier, professor at College de France then at Sorbonne, both in the fields of metallurgy and cements. Although used in the Neolithic era, ceramics were made in a much more rational manner, leading to a broad diversity of properties and applications. A better understanding of these materials, in which defects are, at the same time, a major disadvantage and a source of original behavior, led to solid-state chemistry, which appeared as a mature discipline at a Bordeaux congress held in 1964. From "hard", "shake and bake" chemistry, it became a tailored, "soft" chemistry, thanks, in particular, to the work of Rouxel and Livage, who approached this new world either with the chemical treatment of preformed materials or the stepwise and controlled synthesis from molecular species in solution. Again, natural structures and synthetic products are intrinsically linked through replication of constructions like the silica architectures of diatoma! A complementary approach relates to microporous materials, sources of "shape-selective" catalysts, membranes, and, even in its latest achievements, traps and reservoirs for molecular species.

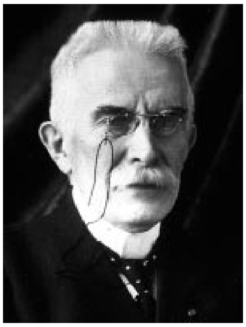
The identification of new sources of natural products that have astonishing structures with an impressive number of chiral centers shows the immense diversity of the molecular, macromolecular, and inorganic structures. An Alsatian, Werner, by proposing spatial arrangements of molecular entities around a metal cation to describe coordination complexes, laid the foundations of organization at a supramolecular level. Another Alsatian, Lehn, developed this concept, leading in a rational way to supramolecular chemistry with auto-organization and then self-assembly of increasingly complex entities. Nature, while being based on the multiplicity of ion–ion, ion–molecule, and molecule–molecule interaction modes, exploits this concept with increasing complexity, leading finally to living organisms capable of self-replication. Supramolecular chemistry suggests that if these interactions can be broken in the same way as they are made, a genuine constitutional dynamic chemistry would be in operation, providing original structures capable of auto-repair, another property related to all living things.

Many of these developments would not have taken place if the structure of the organic molecule had not been understood. In 1858, Kekulé proposed to describe organic molecules by their carbonaceous sequence, the carbon atom being tetravalent. The same year, Couper, who worked in the Wurtz laboratory in Paris, presented at the young "Société Chimique de Paris" his ideas on the "forces of attraction" that exist between the various elements of an organic molecule, what we call now bonds between atoms. The Couper formulae were used by Meyer in Germany, then by Boutleroff in France, who proposed the term "chemical structure" in 1864 "to indicate the chemical sequence or the way in which the atoms are connected" in a molecule. In the same year, modern chemical writing was introduced, thanks to Brown who depicted the atoms by their symbols and each connection by a continuous line. In 1874, the tetrahedral image of carbon was proposed by van't Hoff and Le Bel, hence opening the way to the three-dimensional representations of organic molecules. Thus, we can understand why apparently identical molecules are in fact dissymmetrical and deflect light differently. If "only the products born under the influence of Life are dissymmetrical", then "all the molecules prepared in our laboratories are symmetrical", said Pasteur. However, in 1894, Fischer, who studied the stereospecificity of enzymes, deduced from his observations the structural "key−lock" relationship between a sugar and its enzyme. Prelog, Kagan, and many others used all the subtlety of asymmetric synthesis, then of enantioselective catalysis, to obtain man-made optically active compounds.

We have such a clear vision of atoms in our mind that we may have forgotten how strong the opposition was to atoms in France during the 19th century. At that time, atoms were a theoretical concept introduced by Dalton at the beginning of the 19th century, and this concept was adopted by the whole chemistry community during the Karlsruhe meeting in September 1860. In 1877, the Academy of Sciences was the witness of a violent controversy between Berthelot, opposed to, and Wurtz, defender of atomism. Wurtz and his many students employed the "Société Chimique de Paris" and its Bulletin as a mighty place for defending atomism in France, which gradually enabled the conversion of French chemists to this theory. Bohr applied the quantum theory to the planetary model of the atom proposed by Rutherford in 1911. To describe chemical bonding Lewis and Kossel developed, in 1916, the octet relationship, based upon the outer electrons. Hückel in Germany and Mulliken in the United States introduced molecular orbitals; however, Pauling is the true holder of this new approach, by introducing the notion of hybridization of carbon orbitals in a paper issued in 1931, and by publishing his famous book: "The Nature of the Chemical Bond" in 1939. If this era represents the golden age of the covalent bond, then other interactions were already taken into account: from dative bonds, first introduced by Werner, to the generalization of Lewis interactions, to weaker interactions like van der Waals forces present in soft matter. The importance of the hydrogen bond, exemplified by Pimentel's work, strongly contributed to the understanding of interactions occurring in biological systems: let us recall that the DNA structure is controlled by hydrogen bonds, which are also present in supramolecular chemistry. In addition to this diversity of bonding modes, the introduction of new concepts and the improvement of mathematical methods and data-processing led to descriptive and predictive tools for these connections and the resulting properties. Forty years after the foundations were set down by Schrödinger, the work of Hartree and Fock, Kohn and Pople have provided tools like density functional theory (DFT), now unavoidable for the understanding of physical and chemical properties.

Jean-Marie Lehn

Louis Pasteur



Henry Le Châtelier

Parallel to the development of this writing that makes chemistry a science which has its own alphabet, the desire of comprehension of the chemical reactivity was also very strong. Following the seminal works of Carnot, Kelvin, and Clausius, the development of thermodynamics led to the birth of physical chemistry — a junction of chemistry and physics — exemplified by Le Châtelier, Gibbs, Arrhenius, van't Hoff, and Ostwald, who often were chemists as much as they were physicists: Didn't Ostwald develop the ammonia oxidation process? It is worth noting the subtle differences that have appeared since between physical chemistry and chemical physics, if one considers the microscopic and now nanoscopic domains at which new chemical reactivity is being born. Physical chemistry, like analytical sciences, irrigates all the disciplines of chemistry, and the younger generations often neglect its importance; it is, for example, behind the classification of fundamental reactions of organic chemistry established by Ingold!

All these advancements could not have been done without a panoply of analytical tools pushing back the limits of detection and temporal scales of observation for more than two centuries. Centesimal analysis introduced after the works of Lavoisier and Priestley by Gay-Lussac and Thenard, Berzelius, Dumas, Liebig, and Pregl, to quote only the major contributors, was supplemented by isotopic analysis and determination of exact masses by high-resolution mass spectrometry. Separative analysis experienced extraordinary developments following the invention of chromatography by Tswett, a Russian botanist with a predestined name. If we had to wait until 1931 for the work of Kuhn on the separation of carotenes, then the post-war period saw the systematic recourse to this technique and its numerous alternatives, crowned by the Nobel Prize of Sanger in 1958. The pharmaceutical industry even exploits Tswett's technique to obtain optically active molecules from racemates.

Emission and absorption spectroscopy can be applied to an extremely broad frequency range, providing information on the structure and the movement of the chemical objects. This development goes hand in hand with a growing mastery of technology: in 1939, Beckmann introduced the first UV/Vis spectrophotometer, which enabled Woodward to achieve his PhD within one year − the first of the Woodward rules. The advancement of mass spectrometry led to considerable achievements as a spin off of the Manhattan project. In the same way, the rise in the use of increasingly high radio frequencies and intense magnetic fields benefited resonance spectroscopy, leading to the emergence, for example, of 1 GHz NMR spectrometers able to solve the structure of proteins of several tens of thousands of daltons. Lastly, the current data-processing resources has made it possible to systematize the use of Fourier transform with respect to NMR, IR, and EPR spectroscopy, mass spectrometry, and so forth. The discovery of X-rays on the eve of the 20th century has also contributed to the knowledge of the crystalline structure of increasingly complex molecules. In fact, the development of intense and focused sources (synchrotron radiation), two-dimensional detectors (a consequence of Charpak's work), and powerful computational tools supplements the spectroscopic studies of molecules and macromolecules.

As never satisfied, the chemist also seeks to directly see the object of his studies. The development of magnetic lenses has allowed the visualization of nanometric and sub-nanometric objects by electron microscopy. Scanning electron microscopy is of primary importance for the development of materials and the study of their behavior. A new stage was reached with the work of Rohrer and Binning on scanning tunnelling microscopy (STM) and its derivatives, which allows not only the observation at atomic scale, but also writing on this scale with atoms. The last achievement in microscopy techniques, recently developed by Zewail, takes advantage of laser coherent electron packets generated with femtosecond laser pulses. The combination of spatial and temporal dimensions makes possible the analysis of the dynamic structure of inorganic, organic, and biological materials without damaging the objects by high-resolution electron microscopy.


Joseph Fourier

This extraordinary rise in laser technology largely opened the field of the studies including time as the fourth dimension in chemistry. The exploration of the "Femtoland" by Zewail, associated to the modeling of the processes studied, offers extraordinary prospects for the comprehension of chemical reactivity. Other methodologies, with other timescales, also make it possible to access various types of chemical events. Thus, cyclic voltammetry at very high scanning rates contributes to the mechanistic studies of electroactive systems; synchrotron radiation allows time-resolved diffraction experiments, and so forth.

Will we attend the birth of a virtual chemistry? It should be hoped that it does nothing but supplement the pallet of chemistry now extending to constitutional dynamic chemistry. To return to Berthelot, in conclusion, let us recall his remark: "the chemist creates the object of his study". The objects become only more complex and offer a promising future to chemistry and to chemists.

Acknowledgments

We wish to acknowledge the members of Club d'Histoire de la Chimie and the writers of numerous biographies of former presidents of the "Société Française de Chimie".