Auguste Laurent. Radical and radicals

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ABSTRACT
Auguste Laurent (1807-1853) was one of the most important chemists of the nineteenth century. He discovered and synthesized a large number of aromatic organic compounds, among them naphthalene derivatives, anthracene, phenanthrene, stilbene, benzil, phthalic acid, phthalic anhydride, and pyrene. His theories about equivalents and radicals were fundamental for destroying the dualistic approach and establish the modern approach of organic chemistry. He proposed a new rational method of organic classification based on the functional groups present in the molecule that became the basis of the Geneva nomenclature for organic chemistry adopted in 1892. His radical political ideas and his acrid commentaries on the opinion and errors of fellow chemists curbed his academic progress and were an important reason for the poor reception of his advanced ideas during his lifetime.

KEYWORDS: Naphthalene and derivatives, phthalic acid, coal tar distillation, radicals, type theory, chemical classification and rules

Resumen (Augusto Laurent. Radical y radicales)
Auguste Laurent (1807-1853) fue uno de los químicos más importantes del siglo diecinueve. Fue responsable del descubrimiento y la síntesis de un gran número de compuestos orgánicos aromáticos, entre ellos derivados del naftaleno, antraceno, fenantreno, estilbeno, benzil, ácido ftálico, anhídrido ftálico y pireno. Sus teorías sobre los equivalentes y los radicales fueron fundamentales para destronar el enfoque dualista y establecer el enfoque moderno de la química orgánica. Propuso un nuevo método racional de clasificación orgánica, basado en los grupos funcionales característicos presentes en la molécula, que fue la base de la nomenclatura de Ginebra para la química orgánica, adoptada en 1892. Sus ideas políticas radicales y sus ácidos comentarios sobre las opiniones y errores de otros químicos frenaron su avance académico y fueron una razón importante para que sus avanzadas ideas no fueran reconocidas adecuadamente en su tiempo.

Life and career
Auguste (Augustin) Laurent was born on November 14, 1807, in Folie (today St.-Maurice-les-Langres), near Langres, Haute Marne, the second of the four sons of Jean Baptiste Laurent, a wholesale wine merchant and farmer, and Marie-Jeanne Maître, the daughter of a merchant from Burgundy. His parents passed away when he was very young. Laurent early attracted the attention of his teachers, who persuaded his father and then his maternal uncle, to let him proceed to higher studies (Potter, 1953). After completing traditional classical studies at the collège of Gray he passed the entrance examination for the École des Mines in Paris and was admitted in 1826. During the summer of 1828 he made a study trip to Germany to learn the techniques used in the cobalt mines. The results of this visit were the subject of a thesis submitted together with Guy Adolphe Arrault (1806-), a fellow student, in partial fulfillment of the requirements for the degree ingénieur des mines (granted to him on December 20, 1830), and also of his first publication (Arrault and Laurent, 1830; Jacques, 1954).

In 1831, instead of taking an industrial job or becoming a civil servant, Laurent followed his scientific inclinations and accepted the position of répétiteur (lecture assistant) for the course given by Jean-Baptiste André Dumas (1800-1884) at the École Centrale des Arts et Manufactures. There he became an expert experimentalist and dedicated himself to research. Already in 1832 he published with Dumas his first memoir on naphthalene that he isolated from coal tar (Laurent, 1832). He quitted his job in 1832 after having his first misunderstandings with Dumas, and accepted the position of directeur des essais chimiques (chief analyst) at the Sèvres Porcelain Factory, which was directed by Alexandre Brongniart (1770-1847), Dumas’s brother in law. At Sèvres he familiarized himself with the chemistry of silicates and developed a method for the analysis of alkaline silicates, simpler and more precise than the ones used then, involving treatment with hydrofluoric acid. It consisted basically of preparing the acid in a platinum tube and directing the fumes produced into the silicate sample. The fluoride generated was then converted into sulfate, and the latter dried completely. The following steps were the standard ones for a sulfate mineral (Laurent, 1835b).

Interested in gaining his independence he became a partner in an industry manufacturing cupric sulfate and also opened a small private school for paying students; both initia-
In 1836 he worked for a short time as a friend, the Parisian perfume manufacturer Ed. Laugier, distilling essences. While at Laugier’s, he began his work for the degree of doctorat-ès-sciences, which led to the granting of the degree of bachelor and licencié (October 31, 1837) and to the successful defence of his doctoral thesis at the Sorbonne on December 28, 1837, in front of a committee composed of Pierre-Louis Dulong (1785-1838), César Despretz (1791-1863), and François Sulpice Beudant (1787-1850). According to Stumper (Stumper, 1953) his doctoral theses were two, one entitled Recherches Diverses de Chimie Organique et Sur la Densité des Argiles Mixtes, and the second, Des Considérations Générales sur les Propriétés Physiques de Atomes et sur leur Forme, but Jacques (Jacques, 1954) claims that the actual titles were Recherches Diverses de Chimie Organique et Sur la Densité des Argiles Cuites à Diverses Températures. In the first thesis Laurent developed the principal ideas of his theory of fundamental and derived radicals in organic chemistry and published it as a memoir in Annales de Chimie (Laurent, 1837a).

In 1836, before defending his doctoral thesis, Laurent directed for 18 months a porcelain factory in Eich, near Luxemburg. There he met M.-L. Schrobilgen, councillor of Supreme Court of Justice and on July 23, 1838 he married his daughter, Anne-Francoise (1820-1914). They had a daughter and a son, Mathieu Paul Hermann (1841-1908). Hermann followed a military career, rising to the rank of officer before he resigned in 1865 to devote himself to mathematics where he achieved prominence (Stumper, 1953).

The porcelain factory closed down in 1838 and on November of the same year Laurent moved from Luxemburg to Bordeaux, where he was appointed to the newly created chair of chemistry at the Faculté des Sciences. He held this position for 10 years, during which he published about 100 papers (Stumper, 1953).

In 1846 he worked for some time at the Collège de France and also he gave a free course on chemistry at the Faculté de Médecine. Afterwards he worked at Antoine-Jerôme Balard’s (1802-1876) laboratory in the new École Normale. In 1848 he obtained a modest position as assayer at the Mint (Potter, 1953).

In 1851 Laurent presented his candidature for the chair of chemistry at the Collège de France left vacant by the resignation of Théophile-Jules Pelouze (1807-1867) and defeated François Ernest Balard (1833-1894), the discoverer of bromine [although Justus von Liebig (1803-1883) claimed that Balard was discovered by bromine!] by thirteen votes to nine. This election had to be ratified by the Académie des Sciences. In spite the clear recommendation of the College and the favorable opinion of Jean-Baptiste Biot (1774-1862), the famous physicist (Biot, 1850), the Académie disregarded the advice and voted for Balard (35 to 11), probably a sign of the opposition to Laurent’s radical political and chemical ideas (Stumper, 1953).

Having fallen seriously ill, in 1852 he went to recuperate in the south of France, but died in Paris of tuberculosis on April 15, 1853, and was buried in the Montparnasse cemetery. His family was awarded a state pension. The town of Langres erected a monument in his memory, which was destroyed during the German occupation of 1940-1944, and rebuilt after the war by the town authorities (Stumper, 1953).

In 1845 Laurent was elected Chevalier de Légion d’Honneur and also corresponding member of the Académie des Sciences, replacing Faraday who had been promoted to Foreign Member. In 1849 he became member of the Chemical Society of London. In 1858 the Académie des Sciences awarded posthumously to Laurent and Gerhardt the Jecker Prize for the Advancement of Organic Chemistry (6140 francs to each of the two widows) (Stumper, 1953).

Laurent left unpublished the manuscript of his book Méthode de Chimie, which was edited by François Joseph Jérôme Nicklès (1821-1899) and published posthumously in 1854 with an introduction by Biot, and subsequently translated into English by William Odling (1828-1921) (Potter, 1953).

Scientific activities
The scientific work of Laurent is reflected in more than 200 memoirs and notes and the books Précis de Cristallographie Suivi d’une Méthode Simple d’Analyse au Chalumeau d’Après des Leçons Particulières (Laurent, 1847), Théorie des Radicaux Dérivés et Mémoires sur les Séries Naphthalique et Stilbique (Laurent, 1850), and Méthode de la Chimique (Laurent, 1854). Grimiaux’s book (Grimaux, 1900) contains a copy of a large number of the letters exchanged between Laurent and his close friend and collaborator, Charles-Frédéric Gerhardt (1816-1856). Some of his most significant contributions are described below.

1. Organic chemistry
Laurent first incursions in organic chemistry were his thorough and meticulous experimental investigations of naphthalene and its derivatives. In 1831, Dumas, who was studying the reactions of halogens upon various hydrocarbons (Dumas, 1828-1846), suggested that Laurent undertook the isolation of naphthalene from coal tar, its purification, analysis, and its reaction with the halogens and nitric acid. John Kidd (1775-1851) discovered naphthalene in 1821 when passing coal tar over an incandescent tube (Kidd, 1821), a procedure yielding very small amounts of the compound. Laurent compared several methods of extracting naphthalene from coal tar and found that the yield could be improved significantly if a current of chlorine was passed over fractional distillates of the tar. The resulting process was of low cost and could be used for the commercial production of naphthalene, if a suitable use was found for it. The method was based on Dumas’ opinion that naphthalene exists preformed in coal tar and can be crystallized when the oils that hold it in solution are destroyed (Dumas, 1828-1846). Using the same method Laurent and Dumas discovered anthracene (paranaphthalene) in 1832 (Laurent, 1835a). Analysis of both naphthalene and
anthracene proved that they were hydrocarbons containing the same relative proportions of carbon to hydrogen (5:2). Afterwards, Laurent examined the action of chlorine on naphthalene itself and found two products that he believed were chlorides of naphthalene, one a white crystalline solid, the other an oily liquid, which he assumed to be analogous to the Dutch liquid (ethylene dichloride) on which he had already begun to work (Laurent, 1834; De Milt, 1953). Two years later (1835), after developing the proper special purification and separation steps, he identified three substitution products of naphthalene, the mono-, di-, and tetrachloride. Laurent obtained from naphthalene numerous chloride, bromine, sulfonated and nitrat (NO₂) substitution products and systematically compared their chemical and physical properties (Laurent, 1840, 1842a; Novitski, 1992).

The preparation of naphthalene was followed by a study of its reactions with chlorine, bromine, and nitric and sulfuric acid anhydrides. Laurent prepared nearly 100 new derivatives of naphthalene with these reagents (Laurent, 1832, 1833; Dumas, 1832). His work led to the discovery of anthraquinone, benzil, phthalic acid (with Dumas), phthalic anhydride, and phthalimide, stilbene, diphenyl, isatin, chrysene and pyrene (Laurent, 1837ef). Laurent also prepared the chlorinated and brominated derivatives of cinchonine, the chlorinated derivatives of cinnamene (styrene); established the exact formula of glycoll (glycine), benzidine, studied the essences of bitter almond, rue (Ruta graveolens), estragon, cinnamon, aniline, fatty acids, etc. Between 1835 and 1837 he published several important papers (Laurent, 1835a-h, 1837d) on the benzoyl radical and its derivatives, in which he reported the formation of benzil by the action of chlorine on benzoin, and the conversion of benzil into benzoic acid by the action of strong potassium hydroxide solution, and on derivatives of naphthalene. In 1836 he announced the discovery of a new acid, naphthalique (phthalic) prepared by treating hydrochloride de chloronaphthahlése (naphthalene tetrachloride) with 4-5 times its weight of ordinary nitric acid (Laurent, 1836a). On cooling the solution deposited laminar crystals of phthalic acid hydrate, which by sublimation produced the anhydrous acid. Laurent studied its physical and chemical properties, and believing the resulting substance to be a naphthalene derivative, named it naphthalenic acid. Jean Charles Galissard de Margnac (1817-1894), had already put in doubt the nature of melon as a radical and the existence of melonhydrate (C₆H₅N₂) and ammeline (C₃H₅N₅O). The reaction of melam with sulfuric acid yielded a neutral material Liebig named ammeline, C₆H₅N₉O₃. The reaction between chlorine and ammonium thiocyanate produced another new material, which he named melon and assigned the formula C₅N₄ (Liebig, Wöhler, 1830, 1845). Liebig believed that melon was a radical composed of carbon and nitrogen and played the role of a radical generator of mellonures, in the same way that the cyanogen radical generated the cyanides.

Liebig’s results, which constituted the basis of the theory of composite radicals, were proved to be completely wrong by Laurent and Gerhardt. Gerhardt, in his book Précis de Chimie Organique (Gerhardt, 1844-1845), had already put in doubt the nature of melon as a radical and the existence of melonhydrate and mellonures. He repeated Liebig’s experiments but came to the wrong conclusion that ammeline was actually a previously unknown meluric acid, C₅N₄(NH₂)(OH)₂ (Gerhardt, 1844).

In March 1846, Laurent and Gerhardt read to the Académie a joint memoir in which they proved the many mistakes that Liebig had done in his work, and with their results led to the ruin of Liebig’s theory of radicals (Laurent and Gerhardt, 1846). In the introduction of their paper they repeated the basic tenets of their new theory about chemical equivalents (corresponding to 4 volumes of vapor): (a) The equivalent of every oxygèned substance contains an even number for oxygen and its replacements, (b) In the equivalent of every substance not containing nitrogen the sum of the hydrogen atoms and its replacements (halogens and metals) is a number divisible by four (c) In the equivalent of each nitrogen-containing substance (and or phosphorus and arsenic) the sum of hydrogen, nitrogen atoms (or their replacements) is also a number divisible by four and (d) The equivalent of all carbonated substance always contains always an even number of equivalents of carbon (or divisible by four with C = 73.5). Then they challenged Liebig’s results with
hard words: “The question now is: either our four propositions are incorrect, or Mr. Liebig’s experiences with melon, sulfocyanogen, and their derivatives, are false.”

Laurent and Gerhardt then discussed the preparation, analysis, and formula of the different compounds and concluded that since melon was very difficult to prepare in a very pure form, what Liebig had actually analyzed was an impure sample and had thus reached the wrong conclusions that the compound did not contain hydrogen, that it contained eight atoms of nitrogen, that when heated it decomposed into three volumes of cyanogen and one of nitrogen, and that it should be considered a radical similar to cyanogen. By rigorous chemical analysis Laurent and Gerhardt first proved that the correct formula of melon was \( C_6H_3N_9 \) and that melon could not be considered a radical similar to cyanogen. Their experiments proved the many errors done by Liebig, among them that Liebig’s chlorocyanamide yielded actually the double amount of chlorine claimed by Liebig; that his melam was actually a mixture of melon and an isomer of melamine; that melon did not combine directly with potassium, but the reaction took place with release of ammonia and yielded a dibasic salt; that melon produced by calcinating persulfocyanhydric acid (\( C_3H_2N_6S_3 \)) and dissolved in potash, did not yield melon but a tribasic salt, with the simultaneous release of ammonia; that the cyanic ether reported by Liebig was actually a tribasic salt, with the simultaneous release of ammonia and yielded a dibasic salt; that melon produced by calcinating persulfocyanhydric acid (\( C_3H_2N_6S_3 \)) and dissolved in potash, did not yield melon but a tribasic salt, with the simultaneous release of ammonia; that the cyanic ether reported by Liebig was actually urethane; and finally, that many of the compounds prepared by Liebig were actually cyanamides. In addition, Liebig prepared ammelide and assigned to it the formula \( C_6H_9N_9O_3 \), which Laurent and Gerhardt showed should be \( C_6H_7N_9O_2 \). Liebig and Wöhler also claimed they had obtained a new derivative from urea, to which they assigned the formula proposed by Laurent and Gerhardt to be ammelide. They corrected the formula of ammelide and identified it with the product resulting from the dry distillation of urea.

This paper by Laurent and Gerhardt is an excellent example of the caustic manner in which they used to refer to fellow chemists when they found them in error, and explains why the two young scientists were not held in high esteem by their colleagues, in spite of their significant contribution to the development of chemistry. In this paper (Laurent and Gerhardt, 1846) they refer in these terms to Liebig’s findings: “The researches of Mr. Liebig about these substances constitute one of the strongest pieces of evidence quoted to support the theory of radicals that he teaches at Giesen. Since the gas melon is a radical composed of carbon and nitrogen, melonures correspond to cyanides, and hydromelonic acid to hydrocyanic acid and itself is a sulfocyanogen radical...At the time of our last communication we had not yet considered the full work of Liebig. We had modified only part of the theory, and the authority that the name of Liebig represents, seemed to us enough guarantee for his other results. Today, we regret to communicate to the Academy that this confidence was absolutely deceiving; it is not that part of Liebig’s work is wrong, but so is all the history of melon, sulfocyanogen, all their transformations, and all their reactions. In addition, we are now able to prove that these supposed analogues of cyanogen (melon and sulfocyanogen) do not exist.”

3. The theory of radicals

In 1836, Laurent, then a student of Dumas, carried on the chlorination of ethanol (Laurent, 1836) and gave a fatal blow to Berzelius’ views, for chlorine was considered negative and hydrogen positive, yet one could be substituted for the other without making a drastic change in the properties of a compound. Further experimentation by Laurent showed that radicals were not as indestructible and untouchable as Berzelius insisted, and that one must not overemphasize the matter of positive and negative. Eventually, the dualistic theory lost value and the new views of Laurent took over. In the end, Laurent dropped the concept of electrical forces and assumed that an organic molecule had a nucleus (which might be a single atom) to which different radicals could be attached (Laurent, 1837abc).

In his publications about the chlorination and bromination of naphthalene (Laurent, 1833, 1835c) Laurent stated for the first time his theory of fundamental and derived radicals. He wrote: “Naphthalene forms a radical of 56 atoms or 28 equivalents analogous to ethylene (l’hydrogène bicarbonate). Put into contact with various bodies (chlorine, bromine, and nitric acid), this radical loses hydrogen, but it always gains in exchange one equivalent of chlorine, bromine, or oxygen, in such a way that there is constantly a radical containing 28 equivalents like naphthalene...these new radicals can exist free or combined. The hydrogen which has been removed either disengages or remains combined with the new radical in the state of HCl, HBr, or water...I will call naphthalene a fundamental radical and derived radicals those which are generated by its transformations” (Notvitski, 1992). An essential part of the theory was that the radical always retained its characteristics, independent of the substituents that constituted it (oxygen, hydrogen, nitrogen, chlorine, or bromine) (Laurent, 1837b; Potter, 1953). In other words, Laurent’s concept of fundamental and derived radicals was that all organic compounds could be classified in groups, in which each member originated from the same fundamental hydrocarbon radical and contained the same constant number of carbon atoms. Derived radicals were obtained from the fundamental radical when the hydrogen of the latter was replaced by an equivalent quantity of the dehydrogenating substance (Laurent, 1837b, 1843a; Notvitski, 1992).

The theory about fundamental and derived radicals was given a precise form in Laurent’s doctoral thesis (Laurent, 1837ab). He first described the prevalent ideas among chemists: Although there were many theories, they could be divided into two central ones. One theory postulated that in order for two compounds to react, their molecules had to align side by side to form a new substance in which the atoms of the molecules retained the relative places they had before the reaction. Every chemical substance was formed of two constituents, simple or complex, having opposite electrical
charges. Their mutual attraction determined the coupling act. The two constituents could be separated, or at least recognizable. This dualistic theory postulated that in order to prepare a salt, it was enough to contact a basic oxide with an acid one. The main supporter of the dualistic theory was Jöns Jacob Berzelius (1779-1848). If this representation was easy for a molecule of a simple salt like sodium chloride, composed of positive sodium and negative chlorine, it became very difficult as the salt became more complicated. For example, sulfuric acid combined with one molecule of potassium hydroxide to yield potassium sulfate. In this salt, sulfur remained surrounded by three atoms of oxygen and the potassium atom remained combined with its oxygen atom. In an electric pile the sulfate decomposed into an oxide and an acid, which proved that its formula was $SO_3 + OK$.

Other chemists rejected this explanation on geometrical considerations: How was it possible for a molecule having a certain crystalline form to align itself with a molecule having a different crystalline configuration and generate a third species, having a regular and symmetrical structure, incompatible with that of the original reactants?

In the second theory, the formation of compound bodies was explained assuming that many atoms of one compound united with many atoms of the second one, to form a new molecule, in which the atoms were grouped symmetrically, according to a certain regular geometrical structure, without the need for any particular atom to combine specifically with another.

The dualistic theory was easily extended from inorganic to organic chemistry. An organic substance was composed of two different constituents presenting antagonist properties. Thus alcohol was composed of carbonated hydrogen (ethylene) and water. In this manner alcohol became ethylene hydrate having the binary formula $C_2H_4\cdot O$. Although in inorganic chemistry it was not difficult to establish the formula of a compound, the situation was not the same for organic compounds where the elements had such mobility that the same body presented such a myriad of reactions. In these circumstances it was extremely complicated to determine the antagonist elements. For example, oxamide (oxalic acid diamide) under the influence of sulfuric acid converted into oxalic acid and ammonia, or into cyanogen and water, or into ammonia, carbon dioxide and carbon monoxide. The same behavior was observed with acetic acid, formic acid, alcohol, etc. (Laurent, 1843b)

To overcome these restrictions, Laurent used his strong background in crystallography to suggest a model for substitution reactions. He compared the organic molecules to a prism from which the ridges could be removed and replaced by different ones capable of filling the same geometric space without destroying the primitive form of the crystal. To illustrate his theory Laurent assumed the hydrocarbon $C_{12}H_{12}$, which could be represented by a six-face prism in which each of the 12 solid angles was occupied by one of the 12 carbon atoms and the 12 hydrogen atoms were located at the center of the basal edges. Addition reactions were represented by suspension of pyramids: Two pyramids could surmount these prisms, one on each base. If the pyramid was water, then the formula of the resulting compound would be $Cl_2H_{12} + 2OH_{1/2}$, or $2H_2O$, and could represent an ether or an alcohol. If the pyramids were replaced by others of sulfuric acid, HCl, etc., salts will be formed that could be represented by hexahedral prisms, plus the modification of the bases, that is, $C_{12}H_{12} + SO_3$, $H_2Cl_2$, $N_2O_5$, etc. (Laurent, 1837a).

Laurent had advanced the idea that when chlorine and bromine entered in combination after eliminating their equivalent of hydrogen, they took exactly the same position that hydrogen occupied in the compound and hence both substances, the primitive and the derived one, had to be isomers, (Laurent, 1842b).

In his first memoir about naphthalene, Laurent presented a new compound, which he named chlorobronaphthose, $C_{10}H_8Br_4Cl_4$ (A) obtained by treating naphthalene first with chlorine and then bromine. Reversing the operation he discovered another compound, bromichlonaphthose, $C_{10}H_8Cl_4Br_4$ (A), which although an isomer with the previous one, did not have the same form. Both compounds crystallized as prisms having an oblique base; in the first one the faces were inclined one to the other at $101^\circ30$, $102^\circ50$, and $101^\circ15$ respectively while in the second the angles were $102^\circ30$, $103^\circ00$, and $101^\circ20$. Other examples were chlorobronaphthose, $C_{10}H_8Br_2Cl_6$ (B) crystallizing in six-face prisms, with four angles of $117^\circ30$ and two angles of $125^\circ$; and bromachlonaphthose (B) $C_{10}H_8Cl_2Br_6$ (A and B are isomers) with four angles of $119^\circ$ and two angles of $122^\circ$. Laurent named isomerimorphs those bodies having the same form and the same composition (Laurent, 1842b).

Laurent’s researches on isatin and its chlorinated derivatives clearly demonstrated that negative bodies could replace, in certain combinations, positive bodies without changing in a sensible manner the chemical and physical properties of the compounds. Since chemists had not adopted his opinion yet, he now wanted to demonstrate beyond doubt that chlorine could replace hydrogen, that the original and the new compound were isomorphic, and that the replacement could take place in any proportion, without changing the crystalline form. He wanted to prove that a cube could be isomorphic with a prism having a square or rectangular base, or with an oblique prism, or with a rhombohedron, taking into account that the term isomorphism did not have the same meaning in geometry as in crystallography. In the latter two substances were considered isomorphic when their crystals had more or less the same angles and when they belonged to the same crystalline type. Laurent modified this definition and stated that two crystals were isomorphic when their axes were sensibly equal and sensibly inclined in the same amount, independent of the crystalline type to which they belonged (Laurent, 1845a).

Laurent then proved that it was not necessary for the constituent atoms to be analogues to form analogue compounds; bodies completely different such as chlorine and bromine,
could give birth to compounds having very similar properties, as long as their atoms were arranged in the same manner. In other words, the properties of a compound depended not only on the nature, the number, and the proportion, but also \textit{on the way} their atoms were arranged (Laurent, 1846). He illustrated the latter condition with a geometrical example: Consider two regular polygons, having the same number of edges of the same length, for example, a regular hexagon. If the solid sides were made of different materials, for example iron and copper, it was not enough that each polygon be formed by three sides of iron and three sides of copper for the two polygons to be identical. We could have two regular hexagons of the same nature, same weight and same dimensions, one formed by three neighboring iron sides and three copper neighboring sides, and the other by alternating copper and iron sides. The center of gravity of the first would be the same as the geometrical figure, but not so for the second sample. Hence it was possible to conceive two bodies having the same atoms, united in the same proportion (that is, isomers), with the atoms arranged in the same manner (that is, isomorphs) but as long as the order, that is, the relative arrangement of the atoms was different, then the two bodies would be different. Laurent illustrated his conception in organic chemistry with the following example: Consider two substances containing carbon, hydrogen, oxygen, nitrogen, chlorine, and bromine in the same proportion. The two substances have the same crystalline form, they act on the same way on polarized light; there are two salts having almost the same chemical and biological action. Both cinchonine derivatives were now combined with HCl and HBr in such a manner that the bromocinchonine reacted with HCl and chlorocinchonine with HBr. The two hydracids contained (like the two original bases) four atoms of chlorine or bromine. Two salts were obtained, one containing 4 bromine atoms in its bases and 4 atoms of chlorine in its acids, the other the opposite. Since the two salts had the same composition they were obviously isomorphs. Nevertheless, in spite of their large similarity the two salts were not identical, as could be demonstrated easily with the aid of potash: alkali poured over one of the salts precipitated bromocinchonine and became potassium chloride, while with the other salt, it precipitated chlorocinchonine and formed potassium bromide (Laurent, 1846).

A curious fact is that Laurent, in his thesis and in the related papers, did not mention the fact that André-Marie Ampère (1775-1836) had already looked in detail into the possibility of explaining chemical combinations on the basis of crystallography. 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 geometrical forms were limited to 23. Haüy had already devised the concept of the \textit{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 \textit{before} crystallization; they also kept it when they were dissolved in the caloric, in their gaseous state (the three crystalline states of matter). According to Ampère, 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 octahedrons made up of six molecules of which four came from a hydrogen tetrahedron and two from one half of an oxygen tetrahedron. Hence, the clue to a chemical reaction was to be found on the possibility of superposition of these geometrical figures: “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 vice versa.” (Ampère, 1816; Wisniak 2004).

Ampère’s theory provided little guidance even in relatively simple cases such as water and required the user to be quite knowledgeable in space geometry and 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.

From here on, Laurent developed a non-electrochemical theory of organic reactions based on chlorine substitutions, which he initially called the theory of fundamental and derived radicals. An organic molecule had a nucleus (which might be a single atom) to which different radicals might be attached. Laurent’s theory of fundamental and derived radicals is sometimes known as the \textit{nucleus theory}. He introduced this term in 1842: “It seems that all these compounds have something in common, a fundamental group, or adopting a term from crystallography, a primitive form or core...The cores are not decomposed by heat and alkali. They possess the same shape, as long as there is no dimorphism or polymorphism; they have the same fundamental properties, the same molecular arrangement...” (Laurent, 1842c; Potter, 1953). According to this theory, fundamental radicals could be transformed into derived radicals either by substitution...
within the radical or by addition or elimination of atoms outside the radical. The most important factor for Laurent was not the identity of an atom but its position. The electrochemically opposite hydrogen and chlorine could play the same chemical role inside a radical; but a chlorine atom inside or outside a radical would exhibit different chemical properties. Similarly, oxygen could replace hydrogen inside the radical with no great alteration of properties, but oxygen introduced outside the radical would make a neutral substance acidic.

After Dumas discovered in 1837 trichloroacetic acid (Dumas, 1838) he and Berzelius were forced to accept the substitution theory of Laurent.

In his 1844 memoir (Laurent, 1844) Laurent employed for the first time the word type, which Charles-Frédéric Gerhardt (1816-1856) would use later to propose the theory of types. Organic molecules were now grouped into families or types. All the members of one type would have an identical nucleus to which any of a series of similar radicals could be attached; and within the radicals there would be considerable room for variation. A particular molecular type might even extend into the realm of the inorganic. According to Gerhardt, in the present state of science it was possible to organize organic compounds into three or four types, each one susceptible of yielding a series similar to those formed by a similar nucleus to which any of a series of similar radicals could be attached.

The resounding demonstration of Laurent and Gerhardt’s ideas about the nature of radicals was provided in 1853 by Wurtz’s discovery of mixed radicals (Würtz, 1853), a fact that already been predicted by Gerhardt and Gustave-Charles Bonaventure Chancel (1822-1890) (Gerhardt and Chancel, 1851).

The discovery of mixed radicals signalled total victory of the new theory over the dualistic one.

4. Atomic structure, formulas, and classification
During the eighteenth century the vegetable and the animal themes of chemistry were united under the subject organic chemistry. Chemistry was now composed of two branches, mineral and organic chemistry, according to the distinctive origin of compounds. Later, physiological chemistry was added, which, in France, Charles-Adolph Wurtz (1817-1884) converted into biochemical chemistry in 1874 with the creation of a specific laboratory of chimie biologique at the Faculty of Medicine (Carneiro, 1993). According to Louis-Bernard Guyton de Morveau (1737-1816) by 1760 scientists were familiar with a very small number of compounds. Six acids were known, together two soluble earths, eleven metallic substances, and about thirty salts. Although the actual number was larger, it was still a small fraction of what would be known by the end of next century. The name of each compound was related to their aspect, their origin, a typical property, or the name of its discoverer. The increase in the number of new compounds that took place in the following twenty years created an inextricable confusion in their identification and the appearance of many synonyms. Many chemists had tried to put some order in this anarchic situation by grouping together substances that had the same kinship, particularly the salts derived from the same acid. Guyton proposed the first general nomenclature that led eventually to the one accepted nowadays. In his famous memoir on the subject (Guyton de Morveau, 1787) he established the following principles for assigning a name to a substance: (a) each substance must have a name and use of circumlocutions should be avoided; (b) the name of a compound should reflect the composing parts and characterize it clearly; (c) substances of unknown composition should be assigned a name having no meaning than any other that would convey a false idea; and (d) new names should be based on old languages, such as Latin. As seen above, Guyton’s proposals were concerned almost exclusively with the naming of acids, bases, and salts.

Guyton’s ideas were accepted and supported by most of the chemists of his time [such as Torbern Olof Bergman (1735-1784), Claude-Louis Berthollet (1748-1822), Felice Fontana (1730-1805), Antoine-François Fourcroy (1750-1809), Richard Kirwan (1733-1812), and Pierre-Joseph Macquer (1718-1784), and attacked by a few others [such as Jean-Claude La Métherie (1743-1817) and Balthazar-Georges Sage (1740-1824)] on the arguments that it was “barbarian, incomprehensible, and without etymology”. Eventually Guyton’s classification became essentially official after it was presented to the Académie des Sciences as the book Méthode de Nomenclature Chimique (Guyton de Morveau, 1787), signed simultaneously by Guyton, Berthollet, Fourcroy, and Lavoisier.

In the middle of the nineteenth century the number of organic compounds being discovered was growing very fast and many cumbersome methods were being proposed to move through the myriad of names by which they were known. Laurent was the first to try a logical classification using as a starting point his theory of fundamental and compound radicals, and thus attaching the chemical species to a generating hydrocarbon (Laurent, 1844). According to him “all chemical combinations derive from a hydrocarbon, a fundamental radical, that not always is present in its combinations but is represented by a derived radical containing the same amount of carbon.” Laurent’s idea was to arrange all known compounds in series ordered after the fundamental carbon and constituted the first attempt of a rational classification of organic compounds related to the generating hydrocarbons. At the same time it was in bold opposition to the complex formulas that Berzelius had built following his electrochemical theory. In his memoir, read to the Académie des Sciences, Laurent presented the formative skeleton of his proposed classification. The first division was composed of the four series: (1) Noyaux (nucleus), susceptible of augmentation but not of diminution, which included the ethenides (which formed with acids salts similar to the ethers) ammonides (forming salts similar to those of ammonia), and the analcides (which did not combine with acids and sub-divided into halides, nitriles, and camphides); (2) protogénides, which
subdivided into hydrides, hyperhalides, anhydrides, and aldehydes; (3) sels (salts), which sub-divided into mono- and dibasic; and (4) prométallides.

Laurent’s ideas were fought by Berzelius, Dumas, Liebig (Dumas and Liebig, 1837), and by all those belonging to the scientific establishment, that is, by those who supported a classification of organic compounds according to their origins into resins, fats, essences, and indifferent substances.

Today, the number of organic compounds listed in CAS surpasses 30 million, and their classification is guided in large part by the notion of substitution proposed by Laurent and Dumas, and the notion of homology proposed by Gerhardt. Homology organizes organic compounds in families having an increasing number of carbon atoms and substitution classifies the derivatives of each member of a given family according to the nature of the substituents (halogen derivatives, oxides, nitro compounds, etc.). Laurent’s classification scheme was based on a fundamental radical and its derivatives obtained by substitution and/or addition.

The determination of atomic weights was a crucial problem during the first half of the 19th century, with chemists employing the atomic theory that had been established by Berzelius (Berzelius, 1819). A few others preferred the notion of equivalence; instead of atomic weights they used equivalents, a name introduced by William Hyde Wollaston (1766-1828) in 1814 (Wollaston, 1814). Analysis of matter indicated that simple substances united in definite proportion and multiple proportions. Liebig, Victor Regnault (1810-1878), and Théophile-Jules Pelouze (1807-1867) assigned to carbon a molecular weight of 12 (with H = 1), the same as Berzelius has done previously, while Dumas and his disciples assigned it an atomic weight of 6. Chemistry by itself was unable to fix the relative weight of the atoms, for example, exhaustive analytical tests had proven that hydrogen and oxygen joined in the ratio H/O = 1/8 to form water. If, like done by John Dalton (1766-1844), the formula HO was assumed for water and the weight was assigned to hydrogen, then the proportional number of oxygen became 8. Now, if it was admitted that the formula of water is H2O, then the proportional number for oxygen would be 16, a number valid for all chemical compounds to the weight of two volumes (2 atoms = 1 molecule) Laurent arrived at the first exact definition of molecular weight (Stumper, 1953).

**Miscellaneous**

Laurent synthesized and studied the properties of a very large number of organic compounds. For example, he treated benzaldehyde with aqueous ammonia and after a long time of reaction obtained a colorless substance, insoluble in water, soluble in alcohol and ether, and crystallizing in octahedral of rectangular base. Treatment of the crystals with acetic anhydride and N2H4 for ammonia. In his second memoir he referred the formulas of composite bodies to two volumes of vapor and thus found that the formula of most organic compounds were about one-half larger compared to those of mineral substances, and proposed to half them in order to have their equivalents similar to those of water, carbon dioxide, and ammonia. Laurent in his memoir completed and gave precision to the concepts of atoms and molecules. After adopting, as Gerhardt had done, a common measure of two volumes for composite substances, he extended this viewpoint to the simple bodies, which he considered constituted by an assembly of two atoms. He also distinguished between atoms and molecules and gave the former precise definitions. For him the atom represented the smallest amount of a simple body which could exist in a combination. The molecule represented the smallest amount of a simple body to realize a combination, an amount divisible in two by the act of combination itself. Thus, the atom Cl could well enter into a combination, but to perform it, it was necessary to use the molecule Cl2. Laurent was thus admitting the double decomposition of chlorine by hydrogen to form hydrogen chloride: H2 + Cl2 = 2HCl. This binary atomic association allowed him to also explain the particular affinity exhibited by bodies in the nascent state. By reporting the relative weights of chemical compounds to the weight of two volumes (2 atoms = 1 molecule) Laurent arrived at the first exact definition of molecular weight (Stumper, 1953).
man that leukol and quinoline were identical; thus confirming Laurent’s claims. Laurent analyzed more than 400 nitrogen compounds and found all to satisfy his rule (Blondel-Magrelis, 2001).

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