La química en la historia, para la enseñanza

Charles Fréderic Gerhardt

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Resumen

Charles Fréderic Gerhardt (1816-1856) fue uno de los químicos más importantes del siglo diecinueve, cuyas investigaciones y teorías ejercieron una poderosa influencia en el desarrollo de la química. Su teoría de los tipos fue significativa en impulsar hacia adelante la clasificación orgánica, poniéndola en una forma más racional, y en destronar el enfoque dualista. La teoría de los tipos evolucionó hacia la idea de valencia. Gerhardt generalizó el concepto de homología y equivalentes. Fue asimismo responsable de la síntesis de un gran número de compuestos orgánicos, entre ellos anhidridos y cloruros de ácido, derivados del ácido salicílico, anilidas, y fosfamidas.

Abstract

Charles Fréderic Gerhardt (1816-1856) was one of the most important chemists of the nineteenth century and whose researches and theories exerted a powerful influence in the development of chemistry. His theory of types was significant in pushing organic classification forward, putting it on a more rational form, and in the dethroning of the dualistic approach. The theory of types would eventually develop into the concept of valence. Gerhardt generalized the concept of homologue series and equivalents and was responsible for the synthesis of a large number of organic compounds, among them acid anhydrides and chlorides, salicylic acid derivatives, anilides, and phosphamides.

Life and career (Grimaux,1900)

Charles Fréderic Gerhardt was born on August 21, 1816, in Strasbourg, the son of Samuel Gerhardt (1780-1847) and Charlotte-Henriette Weber (1785-1846). The other two children were Charlotte-Emma (1812-1891) and Gustave-Adolphe (1824-). Hi mother, a widow, brought to the marriage a son,

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Charles-Victor Lobstein (1809-1863). Samuel Gerhardt, born in Switzerland, came from a well-known family of brewers. At a young age he moved to Strasbourg where he found employment in the Turckheim bank and married. His skills led to a fast career and thus to provide his family with a prosperous and cultured home.

Between 1824 and 1831 Charles attended the local *Gymnase Protestant*, an institution controlled by the Lutheran Augsburg Confession. According to Carneiro (1993) the Gymnasium had been founded in 1538 by Jean Sturm (1507-1589), a German Lutheran reformed who advocated and practiced the propagation of knowledge through teaching and publication. This institution was highly regarded in the educational circle; it had resisted several attempts by the Ministry of Instruction to integrate it into the official Lycée program, particularly after the anti clerical atmosphere that was prevalent after the Revolution. The Gymnasium was linked to the Protestant Faculty, which from the previous century had developed a cosmopolitan tradition by attracting European students and professors and whose curriculum integrated music, physical education, languages, and science. Like the majority of the Alsatian bourgeoisie, by enrolling in the Gymnasium, Gerhardt benefited from a bilingual education, which provided access to both French and German cultures. An interesting point is that at the same time that Gerhardt studied in the Gymnasium two other important future French scientists, Herman Kopp (1817-1892) and Charles-Adolph Würtz (1817-1884), were also students there. The three would play significant roles in the understanding of organic chemistry and its reactions.

In 1825, Charles's father, who had made a successful career in the bank, left himself be seduced by the promises of fast and large benefits by a Mr. Schutzembach of Manheim, for the exploitation of a patent for manufacturing white lead. They started an association for this purpose, to which Gerhardt contributed 40,000 francs and Schutzembach the patent and the technical know-how. The construction and operating costs of a factory in Hangenbieten were to be shared equally by the partners. Unfortunately, it soon became clear that Schutzembach was unable to

fulfill his part of the deal and thus Samuel Gerhardt was left with a factory for which he had no technical preparation. An additional sad result was that 22 years later operation of the factory would result in Samuel's death from saturnism (lead poisoning).

In addition to Samuel having to dedicate all of his time pushing the enterprise forward, these events put a tremendous economical stress on the family. It was this situation, which convinced Samuel that his son Charles should acquire the necessary professional and technical education to help in the family business. Thus, in October 1831, the young graduate from the Gymnasium, entered the Karlsruhe Polytechnicum (Institute Polytechnique du Grand-Duchè de Bade), as a free student. This Polytechnicum had been founded in 1825 by the fusion of three specialized institutions and had rapidly acquired a high reputation under the direction of the mineralogist Fréderic-August Walchner (1800-1865). In 1865 it became the *École Supérieure Technique Grand-Ducale* that had for objective the improvement and the propagation of the industrial sciences and arts. The curriculum included mathematics, natural sciences, economic politics, history, and fine arts; it prepared engineers, chemists, foresters, pharmacists, surveyors, and teachers.

The chemistry academic program followed by Charles included inorganic chemistry, theory of salts, organic chemistry, organic acids, basic salts, neutral vegetable substances, wine spirit, ether, and fermentation.

At the end of his studies his father decided to send him to complete his education at the Business School in Leipzig and to study under the direction of Otto-Linné Erdmann (1804-1869), who was then working on the properties of nickel and indigo and the determination of molecular weights and would, eventually, initiate publication of the *Journal für Praktische Chemie*.

Upon his return to Strasbourg Charles devoted all his time and energy to the family enterprises. The white lead factory, the only one in France, was working and producing material that competed very well with the same products imported from Germany and Holland.

The production process was very complicated and costly because of the operational capital needed. The process vessels were earthenware pots, with a false bottom in the lower third. This bottom was filled with vinegar, while the top two thirds were filled with strips of lead sheeting. A layer of these pots were placed on the floor of a shed and surrounded up to the rims with fresh dung or spent tan bark, and urine. The shed was left to heat up by fermentation of the dung and to react for two to three months. The heating evaporated the vinegar and the acetic acid attacked the lead to form various acetates. The carbon dioxide from the decomposition of the dung reacted with lead acetate, forming basic carbonate, (white lead). All these operations required a careful control, be it for the production of carbon dioxide, be it for the temperature that was not supposed to exceed 40°C to avoid the formation of sulfihydrates that gave the product a yellow color. Once the foreman decided that conversion had gone far enough, the stack was carefully broken down and the product first ground and sieved from unchanged lead, then washed to remove any lead acetate and finally dried. All these operations resulted in the formation of large amounts of dust, which had a disastrous effect on the health of the workers. It took a month for washing, another for drying and, in addition, the price of white lead had remained unchanged for over 15 years.

Although Charles could help, he was already suffering the first symptoms of the rheumatic fever that twelve years later would kill him. In addition, Charles's interests laid somewhere else, in pure science and not in monotonous fabrication, on the time lost in small details, etc., to the great deception of his father, after all the sacrifices he had made. Charles was also spending his time in botanical discussions with Frédéric Kirschleger (1804-1869), professor of medical botany at the University of Strasbourg, and attending the public courses given at the *École de Pharmacie* by Jean-François Persoz (1805-1868), Director of the École, and by Charles-Fréderic Oppermann (1806-1872), professor of toxicology, as well as the course given by Louis-Victor Amédée Cailliot (1805-1884) at the *École de Médicine*. In addition, he was secretly doing experimental work. A long paper on the revision of formulas for natural silicates, written in 1834, was accepted by the *Journal für Praktische Chemie* in 1835 when he was only eighteen years old (Gerhardt, 1835). On June 2, 1835, this publication and further research gained him the appointment of corresponding member of the *Société d'Histoire Naturelle de Strasbourg*. This achievement, plain testimony of a clear vocation, produced in his father the opposite reaction that Charles expected. In his absolute intransigence the father could not see his authority unrecognized and, as a consequence, the ruin of

the future plans for his industry. This led to many violent discussions after which Charles abandoned his home.

Without material resources he had no alternative but to request the permission of his father for joining the 13ᵉ lancers regiment at the garrison in Haguenau. The discipline and chores to be served in the army led him to request from his father, to no avail, the appointment of a substitute.[1] Eventually one of his German friends sent him from Dresden the 2,000 francs required for doing so and thus be liberated from his military duties. According to Grimaux it was Charles's father who paid the debt to the friend, through his half-brother Victor, at that time living in Dresden, so that Charles would not know the origin of the money. Grimaux claims that the friend was none other than Justus von Liebig (1803-1883), who then invited Charles to join his laboratory at Giessen.

During the academic year 1836-1837 Charles attended Liebig's lectures and earned his living by translating into French Liebig's book *Introduction à la Étude la Chimie* (Liebig, 1837).

In 1837 Charles decided to abandon Liebig's laboratory and return to Strasbourg in a final attempt to reconcile himself with his father. Liebig provided him with warm letters of recommendation to Persoz and Oppermann at Strasbourg, as well as the draft of his *Traité de Chimie Organique*, with the request that he should find a publisher in Paris for it. After his return from Germany, Gerhardt sent the draft to Théophile-Jules Pelouze (1807-1867) who passed it to the publisher Crochard et Cié with the request to produce a French translation of the same. On inspection of the first proofs Pelouze noted the poor quality of the job done by Plantamour, the translator, and as a result, the job was transferred to V. Masson, who requested the translation from Gerhardt.

The return to the manufacturing facilities of his father was not easy to conciliate with his scientific vocation and the absence of a laboratory. Nevertheless, he succeeded in publishing some original works related to the experiments he had done at Giessen (Gerhardt, 1838a). His father made him a traveling salesman for the industry, a job that discouraged Charles so much that once again he abandoned the parental house.

On October 22, 1838, Gerhardt left for Paris with two francs in his pocket, lent by his half-brother. There he started attending the chemistry courses given by Jean-Baptiste Dumas (1800-1884) at the Sorbonne and Collège de France and the course in physics taught by César Despretz (1791-1863). At the Sorbonne he befriended Henry Sainte-Claire Deville (1818-1881) and Auguste Cahours (1813-1891). Dumas introduced him to Henri-François Gaultier de Claubry (1792-1878), *répétiteur* at the École Polytechnique and publisher of a *Répertoire de Chimie*, who was looking for an editor capable of returning to the publication the fame of which had declined because of gross errors in proof reading. The Répertoire was a periodical reporting for the French public the works of foreign scientists. Immediately with the initiation of Gerhardt's work, Gaultier de Claubry encouraged him by publishing his work on the formula of tartaric acid and organic decompositions (Gerhardt, 1838b). The association lasted only three months because Gaultier de Claubry paid Gerhardt very little on account of the fact that he had added his name as a co-publisher of the journal. Disgusted with the scientific quality of the Repértoire, Gerhardt wrote to Liebig suggesting the publication of another periodical, *Annales des Chimistes Étrangers Paraissant sour les Auspices de MM. Berzelius, Liebig et Graham*, which would report to the French public work done by English and German scientists.

Dumas again came to the help of Gerhardt and obtained for him the position of *préparateur* at a school run by the Jesuits. Simultaneous with all these jobs, Gerhardt continued his studies and in 1839 was granted his *Diplôme de Bachelier ès Lettres* and his *Diplôme de Bachelier ès Sciences Physiques*.

At that time he was finally able to get laboratory space for his chemistry work. Cahours, who was a *préparateur* at the laboratory of Michel-Eugène Chevreul (1786-1889) at the Jardin des Plantes, obtained from his master permission to allow Gerhardt to complete his studies about helenin (C_6H_8O, a colorless crystalline substance obtained from the roots of elecampane, *Inula helenum*, today alantolactone) and succinic acid, as well as collaborate with Cahours's research on essential oils (Gerhardt, 1840, 1841; Gerhardt and Cahours, 1840, 1841).

Gerhardt studied with Dumas for three years and finally became his assistant. Hard work and brilliant research won him in April 6, 1841, the degrees *Diplôme de Licencié ès sciences physiques* and

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[1] In those days it was possible to buy our way out of the army.

Diplòme de Docteur ès sciences physiques. His thesis was on helenin and, among other subjects it contained a series of analyses of picric acid and determination of its correct formula, contradicting the one claimed by Liebig (Gerhardt, 1840, 1841).

Shortly thereafter the position *of chargé de course* at the *Faculté des Sciences* at Montpellier became vacant and Dumas was instrumental in having Gerhardt assigned to it, replacing Antoine-Jerôme Balard (1802-1876), who had moved as assistant professor to the Sorbonne taking the place of Dumas who had been promoted to full professor, replacing Louis-Jacques Thénard (1777-1857).

At Montpellier Gerhardt had to wait three years for the promotion to *professeur titulaire de chimie.* He found the local facilities very limited and so travelled to Paris as often as possible until finally he obtained a leave of absence from Montpellier to work in Paris. In 1851 he requested an additional leave from Montpellier. Although the Rector approved the request, Thénard and the *Counseil Académique* did not and in the end, it was denied. As a result Gerhardt resigned his position and returned to Strasbourg.

In 1844 he began a close friendship with Auguste Laurent (1807-1853), professor of chemistry at Bordeaux, and together in 1845 they established the new journal *Comptes Rendus Mensuels des Travaux Chimiques de l'Étranger*" (Gault, 1956).

To survive, Gerhardt opened an *École de Chimie Pratique* and started writing his monumental *Traité de Chimie Organique*, in four volumes that appeared in 1853-1856, together with a German translation that was published in Leipzig (Gerhardt, 1853-1856). The advertised novelty of the École was its emphasis on laboratory manipulations rather than lectures, thus "completing the theoretical instruction that students received in the public or private chemistry courses of Paris. " The objectives of the École were not only to teach the art of laboratory to the young people who had an interest in sciences, medicine, pharmacy, and industry, but also to provide them with theoretical instruction on general chemistry, organic chemistry, chemical philosophy, etc. The most advanced students would have the means of occupying themselves in research related to the improvement of science and industry and make their results public in a special journal to be published under the name *Journal de Chimie Pratique*. Students were charged 100 francs per month. Gerhardt hired Johann Theobald Silbermann (1806-1865) to teach physics and F. Hautefeuille (E. Kunemann) to teach industrial applica-

tions. The coup d'état of Louis Napoleon (Napoleon III, 1808-1873) on December 2, 1851, was devastating for the enterprise.

In 1855 he was appointed *Chargé des Cours de Chimie* at the Faculté de Sciences and at the *École de Pharmacie* de Strasbourg and in the same year promoted to professeur titulaire de chimie. At the Faculty of Sciences he replaced Louis Pasteur (1822-1895) and Loir at the École de Pharmacie.

At that time he wrote his *Introduction à l'Étude de la Chimie par le Système Unitaire* (Gerhardt, 1844-1845) in which he exposed his new ideas together with those of Alexander Edouard Baudrimont (1806-1880), Marc Antoine Augustin Gaudin, (1804-1880), and Laurent, opposing the dualistic theory. His basic tennets were: "(a) Tous les corps sont considérés comme des molécules uniques et non pas comme des êtres doubles, (b) Nous considerons tout corps simple ou composé comme un système formé par l'assemblage de particules infiniment petites, appelées atomes. Cette système s'apelle la molécule d'un corps, (c) Dans la molécule d'un corps réputé simple, les atomes sont similaires, c'est-à-dire que la science actuelle n'y voit aucune différence. Dans la molécule d'un corps composé les atomes sont hétérogènes" [(a) all compounds should be considered as unique molecules and not as double entities, (b) every simple or composite substance is a system formed by the assembly of infinitely small particles called atoms, (c) in the molecules of a substance considered simple the atoms are similar, that is, science does not see any difference. The atoms in the molecules of a composite substance are heterogeneous] (Gault, 1956).

In 1844 Gerhardt married a Scottish girl, Jane Sanders, with whom he had had three children, Charles (1845-), Gaston-Victor (1848-1872), and Jane-Marguerite (1849-1880).

Gerdhardt died of a sudden fever in August of 1856, before his fortieth birthday. His death was caused by rheumatic fever in his head and the cardiac region, complicated by an acute peritonitis. He had been professor at Strasbourg just 18 months. He was buried in the Saint Hélène cemetery, Paris (Gault, 1956).

Gerhardt politically was a radical and republican in ideas, his career was marked by the profound political and social crisis of his time. He was involved in many scientific disputes with many of the most prominent figures of his time and used a very sharp language to criticize his opponents, including his best

friends. This is the probable reason why it took long to be elected as a corresponding member of the Institute.

Honors and awards

Gerhardt received many honors for his contributions to science. He was member of the Polytechnical Society of Leipzig (1834) and of the Chemical Society of London (1855); corresponding member of the Société du Muséum d'Histoire Naturelle de Strasburg (1835), of the Société Centrale d'Agriculture du Départment d l'Hérault (1841), of the Société Philomatique de Paris (1841), of the Cercle Pharmaceutique du Haut Rhin (1845), of the Société des Sciences Naturelles de Neuchâtel, Switzerland (1847), of the Royal Medical Society of Edinburgh (1849); of the Institut, Paris (1856), and of the Science Society of Rotterdam (1856). He was associate member of Cercle Pharmaceutique de Montpellier (1847); honorary member of the British Medical Society of Paris (1851), of the College of Pharmacy of Philadelphia (1853), and of the British Pharmaceutical Society (1856).

On February 8, 1858, the Académie des Sciences granted Gerhardt posthumously the Jecker prize, for outstanding research in organic chemistry.

Scientific activities (Grimaux, 1900)

The scientific work of Gerhardt is reflected in about 200 notes and memoirs, hundreds of critical analyses published in French and German journals, 9 books and 7 translations of works of Liebig and Berzelius. Gerhardt himself prepared, as was the custom for a candidate to the Institute, a short description of his scientific achievements (Gerhardt, 1850).

His experimental contribution relates to the formula of natural silicates (1835), tartaric acid (1838, 1848), helenin (1840, 1844), essential oils (1840, 1848), valerianic acid (1841), boiling points and the equivalents (1842, 1845), quinoline (1842, 1846), action of sulphuric acid on organic compounds (1843, 1852), phenol (1843), alkaloids (1843, 1849), waxes (1843-1845), mellon (1844, 1847, 1850), anilides (1845, 1848), phosphamides (1845, 1847), pectin (1845), nitrates and nitriles (1845), sulfanilic acid (1845), atomic volumes (1847), orceine and derivatives (1848), leucine (1848, 1850), uric acid derivatives (1848), bitter almond oil (1850), platinamines (1850), acetanilide (1852), acid chlorides and anhydrides (1852-1853), and amides (1852) (Kahane, 1968).

Among his discoveries we can mention cumene, cuminol, cymene, styrene, anilides, sulfanilic acid, acetanilide, etc. He discovered aspirin in the course o his studies of the reactions between anhydrides and phenols (Bercy, 1936). Gerhardt introduced the names phenol, borneol, and glucosides into chemistry.

Gerhardt's first paper was a revision of the formulas for silicates, which he redetermined after exhaustive chemical analyses. He also proposed a methodical classification of this group of complex salts. This memoir was highly praised by Berzelius (Berzelius, 1838).

Gerhardt's second publication, *Sur la Formule Rationelle de l'AcidéTartrique et sur Quelques Décompositions de la Chimie Organique* (Gerhardt, 1838b), also having a theoretical content, was published in the *Répertoire de Chimie*. In it he addressed the formula that must be attributed to anhydrous tartaric acid, which was assumed to be present in tartrates, salts considered to be formed by the juxtaposition of an acid and a base, both anhydrous. Potassium tartrate was thus represented by the formula $[C_8H_8O_{10} + 2KO]$ and tartaric acid was $C_8H_8O_{10}$. According to Gerhardt (Gerhardt, 1838b), the tartaric acid present in tartrates should be represented by $C_8H_4O_{10}$ and not by $C_8H_8O_{10}$ because "toutes les fois qu'une base hydratée décompose un corps organique, cette action a lieu aux dépens des éléments de l'eau, de telle façon que les molécules des corps organiques se groupent de la manière la plus favorable pour former un corps oxygéné d'un côté, un corps hydrogéné de l'autre, indécomposables tous deux à la température à laquelle cette action a lieu" (every time an hydrated base decomposes an organic substance, this action occurs on account of the elements of the water, in such a way that the molecules of the organic compounds group in the most favourable manner to form on the one hand an oxygenated substance, and on the other, the hydrogenated one, both non decomposable at the temperature at which the reaction takes place).

Friedlieb Ferdinand Runge (1795-1867) isolated quinoline from the distillation products of coal and named it leucol or leucine. Gerdhardt had the brilliant idea of comparing two substances, one resulting from the strong pyrolysis of an inanimate raw material, and the other from live matter, and demonstrate the identity between quinoline and leucine (Gerhardt, 1842; Gault, 1956).

1. Mellon and derivatives

Shortly after the publication of his first memoir on anilides (Gerhardt, 1848), Gerhardt occupied himself with the determination of the atomic weight of chlorine and the revision of the formulas of the basic nitrates of copper and lead. Phosphorus nitrides had been described by formulas that did not fit the rules that had been established for nitrogen and phosphorus combinations, and their method of synthesis could not be represented by an equation. The same problem was present in the mellonic combinations found by Liebig.

The known phosphorus nitrides included a phosphide, PN_2, described by Heinrich Rose (1795-1864) (Rose, 1827, 1828), and a compound [PN_2, H_2O], considered as a hydrate of the former and described by Liebig and Wöhler (1830). Gerhardt recognized that the assumed hydrate was actually the amide-amine $PO(NH)(NH_2)$, which could lose water by heating, yielding PN_2H, which he named *phospham*. This first work confirmed the rules established by Laurent and Gerhardt that nitrogenous compounds contained an impair number of atoms of nitrogen and phosphorus.

During his studies of the reactions between potassium thiocyanate with ammonia Liebig came across an insoluble honey-colored product, which he named *melam* and formulated as $C_6H_{10}N$. Heating melam with potassium hydroxide led to the separation of two bases, $C_3H_6N_6$ (melamine) and $C_3H_5N_5O$ (ammeline). The reaction of melam with sulfuric acid yielded a neutral material he called ammelide, $C_6H_9N_9O_3$. The reaction between chlorine and ammonium thiocyanate produced another new material, which he named *mellon* and assigned the formula C_3N_4 (Liebig, Wöhler, 1830, 1845). Liebig believed that mellon 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 constitute the basis of the theory of composite radicals.

Gerhardt, in his book *Precis de Chimie Organique* (Gerhardt, 1840), had put in doubt the nature of mellon as a radical and the existence of mellonhydric acid and mellonures. He repeated Liebig's experiments and came to the wrong conclusion that ammelide was actually a previously unknown melanuric acid, $C_3N_3(NH_2)(OH)_2$ (Gerhardt, 1844) .

In March 1846, Laurent and Gerhardt presented to the Académie a memoir, which led to the ruin of Liebig's theory (Laurent and Gerhardt, 1846). They began by proving that mellon could not be considered a radical similar to cyanogen, they attributed to it the formula $C_6H_3N_9$, and by rigorous analysis demonstrated the numerous errors done by Liebig. They showed that the chlorocyanamide of Liebig yielded actually the double amount of chlorine claimed by Liebig, that mellam was a mixture, that mellon did not combine with potassium, and that the compounds prepared by Liebig must be considered as cyano amides. They corrected the formula of ammelide and identified it with the product resulting from the dry distillation of urea.

Although this scientific problem was of secondary interest, it led to a strong antagonism between Gerdhardt and Liebig (Gault, 1956).

2. Atomic structure, formulas, and classification

In order to evaluate the importance of Gerhardt's work it is necessary to understand the state of chemistry at the time that he initiated his studies under Erdmann and Liebig. Most chemists employed 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. Gay-Lussac's law on the volumetric relations observed in all combinations, the laws of isomorphism, the relations derived by Dulong and Petit between proportional numbers and specific heats, and the wrong-interpreted law of Avogadro and Ampere, where the basis on which Berzelius built his atomic theory, which dominated chemistry between 1821 and 1840. He proposed the dualistic theory based on the phenomenon of electrolysis of salts. For Berzelius, all substances were formed by the union of two groups or two elements, one electronegative and the other electropositive. He admitted that for salts the base and the acid had separate existence; potassium sulfate, for example, resulted from the juxtaposition of anhydrous sulphuric acid and of anhydrous potassium hydroxide. Acids were formed from the acid anhydride and water; replacement of this water by a metal oxide gave place to a salt. Applied to organic chemistry, this viewpoint admitted the existence of an acid anhydride, about which it reasoned but had never been isolated.

Application of this theory by Berzelius to or-

ganic compounds led to the creation of complex formulas in which he assumed the existence of entities, of fictitious groupings, absolutely contrary to the facts about substitution at the root of the works of Laurent and Dumas.

Dumas and Liebig (1837) did the first attempts to write formulas, which were really rational and were tested with the intention of completing the known facts about isomerism of esters, such as ethyl formate and methyl acetate. Dumas considered carbon monoxide as a radical capable of uniting with oxygen or chlorine and believed that methyl oxide and common ether were the monohydrates of hydrocarbons, of which the alcohols were the hydrates. Dumas wrote:

$[C_4H_8, H_2O]$ ethylene monohydrate (common ether)

$[C_4H_8, 2 H_2O]$ ethylene dihydrate (alcohol)

$[C_2H_4, H_2O]$ methylene monohydrate

$[C_2H_4, 2H_2O]$ methylene dihydrate (methanol)

In the same theory chloro ethers (alkyl chlorides) were the hydrochlorides of hydrocarbons, for example $[C_4H_6, H_2Cl_2]$, ethylene chlorohydrate, comparable to ammonia chlorohydrate, $[N_2H_6, H_2Cl_2]$ (ammonium chloride).

In another interpretation, Liebig compared the derivatives of alcohol to the salts of ammonia, in the same way that he considered sal ammoniac as an ammonium chloride, $[N_2H_8, Cl_2]$.

Liebig, Regnault, and Pelouze 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. Anyhow, the atomic theory, as conceived by Berzelius carried within it the germs of its destruction: the confusion between atom and molecules and the basic idea that equal volumes of gases contained the same number of *atoms*. The word atom was employed with different meanings, e.g., physical atom, chemical atom, composite atom of first order, second order, etc.

Equally, there was no law for determining the proportional number in compound substances (what today we call molecular weight). Formulas answered to different volumes of vapors; for non-volatile organic compounds they were simply the translation of their analysis.

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): "Toutes les combinaisons chimiques dérivent d'un hydrogène carboné, radical fondamental, qui souvent n'existe plus dans ses combinaisons, mais qui y est réprésenté par un radical derive renfermant autant de carbone que lui" (all chemical combinations derive from a hydrocarbon, a fundamental radical that does not exist in its combinations but is represented by a derived radical containing the same amount of carbon). It is clear that Laurents idea was to arrange all known compounds in series ordered after the fundamental carbon. This was 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 the Berzelius had built following his electrochemical theory

Laurents ideas were fought by Berzelius, Dumas, Liebig, 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.

The phenomenon of substitution of intensely electropositive hydrogen by intensely electronegative chlorine was considered as a fundamental problem for the theory of electrochemical dualism. For a dualist, all chemical reactions proceeded by addition or separation of two substances, not by substitution of one for another and the glue that held compounds together was electrical polarity.

This was the state of organic chemistry at the time that Gerhardt came into the picture.

A major problem confronting chemists in the early 1840's was whether it was possible to ascertain the arrangement of atoms in a compound. Gerhardt believed that no formula could represent the true composition of substances. It could only represent a certain number of metamorphoses. It was necessary to admit that by formulas we can only express a relative composition and not the absolute arrangement of atoms in the sense of the electrochemical theory. The formulas he wanted to adopt were sort of equations destined to represent the genesis and the metamorphosis that substances experimented (again, Gerhardt used expressions borrowed from the life sciences). Since there were as many equations as metamorphoses, he adopted as an equation the

one that was general and applied to a large number of substances, thus the equations of ethers and amides were similar. In both cases the substances united molecule with molecule with elimination of the same amount of water:

$$C_2H_4O_2 \quad + \quad C_2H_6O \quad = \quad C_4H_8O_2 \quad - \quad H_2O$$
acetic acid alcohol acetic ester
$$C_2H_4O_2 \quad + \quad NH_3 \quad = \quad C_4H_5N \quad - \quad H_2O$$
acetic acid ammonia acetamide
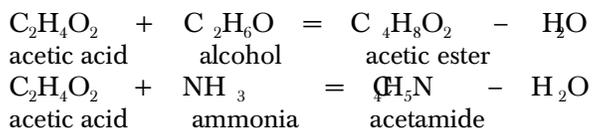
These equations showed the genesis of acetic ester and acetamide and these, by generating the elements of water, reproduced their progenitors.

After Gerhardt's nomination as *chargé de cours* at the Faculty in Montpellier, he devoted part of his efforts to find the appropriate procedures for determining the proportional numbers of organic compounds (equivalents). His first memoir was related to establishing the relations between the formulas and the boiling point of hydrocarbons, an unsuccessful and incomplete effort (Gerhardt, 1845).

The following memoirs (Gerhardt, 1841, 1843) were very significant. It was an attempt to reform atomic and molecular weights, a doctrine that would eventually disentangle the chaos in organic chemistry, and was to be applied also to inorganic compounds. Gerhardt wrote: "L'équivalent de l'eau, tel qu'il faux dorénavant l'admettre, fait disparaitre certaines anomalies bizarres qui existent entre la théorie des volumes, la théorie atomique, et la théorie des équivalents. En effet, d'aprés les deux premières, l'eau se compose de 2 volumes d'hydrogène; la théorie des équivalents, au contraire, dit que l'eau se compose d'équivalents égaux d'oxygène et d'hydrogène, de sorte que 1 volume ou atome d'oxygène correspond à 1 équivalent d'oxygène, tandis que 2 volumes ou atomes d'hydrogène ne correspondent aussi qu'à 1 équivalent d'hydrogène. Nous disons que l'eau renferme 2 équivalents, ou atomes, ou volumes d'hydrogène et 1 équivalent, ou atome, ou volume d'oxygène: sa formule doit être H_2O, H étant 12.5 et O étant 200" (the equivalent of water, such as one should admit, eliminates certain bizarre anomalies existing between the theory of volumes, the atomic theory, and the theory of equivalents. As a matter of fact, according to the first two of them, water is composed of two volumes of hydrogen, while according to the theory of equivalents it is composed of the same number of equivalents of oxygen and hydrogen, so that one volume or atom of oxygen corresponds to one equivalent of oxygen while two volumes or atoms of hydrogen correspond only to one equivalent of hydrogen.We assume that water comprises two equivalents or atoms or volumes of hydrogen and one equivalent, or atom, or volume of oxygen: its formula must then be H_2O, with H equal to 12.5 and oxygen to 200).

The session of the Académie des Sciences (September 5, 1842) where Gerhardt's first memoir was read, was very tempestuous. Thénard argued that the conclusions were of a style that did not fit Lavoisier, Dumas would have liked to eliminate completely the theoretical part, for which the Académie had the monopole, and Victor Regnault (1810-1878) was furious because his formulas had proven to be false.

Gerhardt named his theory "unitary system", by so indicating that it was hostile to the dualistic theory, that the formulas were one and not distributed into radicals and couples, as proposed by Berzelius. His basic tenets were later expressed in the introduction to his book *Precis de Chimie Organique* (Gerhardt, 1844-1845), as follows: "Dans le système dont je propose l'adoption, tous les corps sont considérés comme des molécules uniques, dont les atomes sont disposés dans un ordre déterminé que la réaction chimique n'indique que d'une manière relative. Le système dualistique assimile, au contraire, tou les corps de la chimie à des êtres doubles semblables aux oxydes ou aux sels, et attribue une valeur absolue aux formules qui en répresentent la composition…Le systeme dualistique donne le nom de sels aux corps qui se composent d'un acide et d'une base, sauf les exceptions aussi nombreuses que les cas suivant la règle. Dans le système unitaire, on apelle sel tout corps renfermant un métal qui peut s'échanger par double decomposition contre un autre métal, c'est-à-dire tout corps capable d'éprouver telle ou telle metamorphose charactéristique" (In the system I propose to adopt, all substances are considered as unique molecules in which the atoms are arranged in a given order indicated by the chemical reaction only in a relative manner. On the contrary, the dualistic system assimilates all the chemical substances into double entities similar to oxides or salts and attributes an absolute value to the formulas that represent their composition…The dualistic system gives the name salt to the substances composed of an acid and a base, except that the exceptions to the rule are more numerous than the cases that follow it. In the unitary system the name salt is given

to a substance containing a metal, which can interchange with another metal by double decomposition, that is, every substance capable experience this or other characteristic metamorphosis). Gerhardt argued that the only way to achieve consistency was either to double all two-volume inorganic formulas or to halve all four-volume organic formulas.

We see then that for Gerhardt every reaction was a double decomposition, for example, when chlorine reacted with hydrogen it was the double decomposition of both components to yield HCl + HCl. A double decomposition was the most common reaction in chemistry, perhaps the general form of all metamorphoses, the one preferred over all others for the construction of rational formulas.

In 1848 Gerhardt published his *Introduction a l'Étude de la Chimie par le Systéme Unitaire* (1844-1845), written in Montpellier. There he defined an atom as the smallest amount of a simple substance that can exist in a combination. A molecule was the smallest amount of a simple substance that was necessary to employ to carry on a combination, a quantity that must divisible by 2 by the act of combination. It was Gerhardt's idea that no formula can give the true composition of a compound. It could only relate to a certain number of metamorphoses: "A notre avis, il faut complétement modifier nos idées sur la constitution des corps, et admettre qu'on ne peut exprimer par des formulas qu'un constitution relative, et non un arrangement absolu des atomes dans le sens de la théorie électrochimique" (in our opinion, it is absolutely necessary to modify our ideas regarding the constitution of substances and to admit that formulas can only express a relative composition and not an absolute arrangement of atoms in the sense of the electrochemical theory).

In 1860, four years after the death of Gerhardt, a Congress of Chemistry was held at Karlsruhe to try to put an end to the confusion that prevailed in the different systems of formula followed by different chemists in Europe. These were divided in two camps: those following the old masters, Berzelius, Dumas, and Liebig, representing classical and official science, and the innovators, which were propagating the new ideas of Gerhardt and Laurent. Stanislaus Cannizzaro (1826-1910), who attended the Congress, said: "The habits of mind are often the greatest obstacle to the progress of science. Dumas, accustomed to exalt the whole the work of Lavoisier, for whom he had a patriotic cult, and accustomed to consider the dualistic composition of salts as one of the pivots of science, believed that acceptance of Gerhardt's unitary system was an offense to Lavoisier's memory."

"But, the classifications adopted up to now, do not answer the very principles on which a satisfactory classification must be based. Therefore, it is illusory to want to distribute organic substances according to some of their physical characteristics and to distinguish, for example, fatty substances, essential oils, resins, and colorants, because there are substances that are at the same time fatty, volatile, and acid, or fats, fixed or neutral; or, volatile, fat and alkaline… In a classification that coordinates and predicts at the same time all possible cases, also applicable to future scientific discoveries, one should order substances according to their chemical kinship, to classify them without relation to their acid or alkaline properties, and to group them according to their mode of formation or decomposition in series, or, using the ideas of biologists, according to natural families. Finally, it is a must that the construction of such a scale be such that it indicates for each substance, which are the products that can result by means oxidation and which can be obtained by way of reduction) (Gault, 1956).

3. Homologues

In the introduction of his book *Précis de Chimie Organique* (1844-1845) Gerhardt wrote that consideration of organic matter indicates that they show successive and almost imperceptible gradations so as to form an immense scale, whose upper extreme is occupied by albumin, fibrin, and other complex materials composing brain matter, while at the lower end we find carbon dioxide, water, and ammonia, just above which come formic acid, wood spirit, and their derivatives. The chemist can descend the stairs by burning the upper echelons, or can climb it applying to organic substances reduction processes. Immediately thereafter, Gerhardt defined his theory of homology: "We call substances homologues when they exhibit the same chemical properties and when there are analogies in the relative proportions of their elements" (Gerhardt, 1843).

Compounds having similar functions, like methanol, ethanol, and amyl alcohol, presented the same ratio between carbon and hydrogen: when water was removed from their gross formula they differed by CH_2:

$$CH_2 + H_2O \quad \text{methanol}$$

$C_2H_4 + H_2O$ ethanol
$C_5H_{10} + H_2O$ amyl alcohol
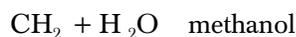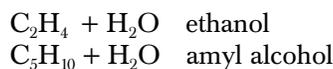
The same relation took place in the fatty acids: removal of the oxygen left carbon and hydrogen in the ratio C to H_2:

CH_2O_2 formic acid
$C_2H_4O_2$ acetic acid
$C_5H_{10}O_2$ valeric acid
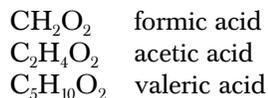
Similarly, alkyl chlorides (éthers chlorhydriques) deprived of the elements of HCl, also contained carbon and hydrogen in the ratio C to H_2:

CH_2, HCl methyl chloride
C_2H_4, HCl ethyl chloride
C_5H_{10}, HCl amyl chloride
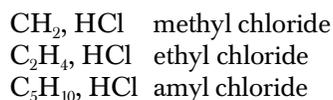
As mentioned above, Gerhardt had named these substances, differing by nCH_2, having the same chemical properties, and fulfilling the same functions, homologues. Although Schiel in 1842 had indicated the relation for the alcohols and Dumas, in the same period, for the fatty acids, Gerhardt was the first to generalize it and establish its importance, not only because they provided a method of classification, but also because they also allowed predicting the existence, the composition, and properties of compounds yet to be synthesized (Gerhardt, 1845). Thus an alcohol must correspond to butyric acid. Equally important, for the first time it was possible to represent organic compounds by a general formula. If, for example, R designated nCH_2 then alcohols would be $R_{+2}O$ and RO_2 would be the acids of the formic series. For the acids containing less hydrogen than CH_2 the ratio R would be followed by a sign minus. Thus oxalic acid, succinic acid, etc., would be within the formula R_2O_4. Furthermore, their respective oxidation, sulfonation, and halogenation products could all be denoted by formulas in which, again, the characteristic (CH_2) unit recurred.

Gerhardt introduced his concepts of homology into his *Précis de Chimie Organique* (1844) with particular reference to the four known alcohols.

4. Radicals

During the 1830's the attempt to model the structure of organic compounds on the dualistic structure of inorganic compounds led to the postulation of a large number of hypothetical radicals, supposedly analogues of the inorganic elements. At a given moment Gerhardt had counted more than 190 of these moieties and remarked sarcastically that new radicals were born everyday. According to Liebig's famous definition, organic chemistry differed from inorganic chemistry in that it dealt with compounds rather than simple radicals. The radical hypothesis presented some difficulties in interpreting known phenomena using the electrochemical theory. The dualistic theory assumed that molecules possessed an electrically positive and an electrically negative part, hence, how was it possible to explain that two hydrogen atoms could unit to become a hydrogen molecule?

Dumas was an enthusiastic supporter of Berzelius; in 1837 he and Liebig published their famous paper on the radical theory in which they boldly declared that all that was needed to be known can be explained by radical theory and that "in mineral chemistry the radicals are simple; in organic chemistry the radicals are compound; that is all the difference. The laws of combination and reactions are, otherwise, the same in these two branches of science" (Dumas-Liebig, 1837).

Gerhardt occupied himself on the equivalence of radicals and exposed ideas which would later be called the atomicity or valence of radicals: radicals that replaced one hydrogen atom in water, like ethyl, were called monatomic because they replaced in the types one equivalent of hydrogen, while the sulfuryl radical SO_2 was diatomic and the phosphoryl was triatomic. He then defined the homologue radicals, differing between them by nCH_2, where n was an integer, and that by substitution of hydrogen in the types gave place to homologue compounds: "Les radicals les plus connus peuvent se représenter par les formules générales suivante (the best known radicals can be represented by the following general formulas):

Monatomic radicals
C_nH_{2n+1} Alcohols
C_nH_{2n-7} "
C_nH_{2n-1} Aldehyde
C_nH_{2n-9} "
$C_nH_{2n-1}O$ Monacid
$C_nH_{2n-3}O$ "
$C_nH_{2n-9}O$ "
$C_nH_{2n-1}O_2$ Dibasic acid
Diatomic radicals
$C_nH_{2n-4}O_2$ Dibasic acid
$C_nH_{2n-12}O_2$ "
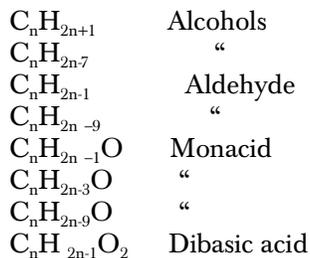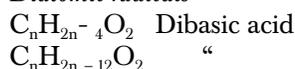
In the 1840's Hermann Kolbe (1818-1884) and Edward Frankland (1825-1899) isolated what they thought were the methyl (CH_3) and ethyl (C_2H_5) radicals (1848,1849, 1850, 1852) and thus appeared to corroborate the analogy between metal and radical. Gerhardt fought against these findings and claimed that methyl does not exist and Frankland's radical must be represented as its dimer, C_2H_6 (ethane). He based his argument on an irrefutable experimental fact: the assumed methyl treated with chlorine yielded a chlorinated gas C_2H_5Cl. Another of Frankland's findings confirmed Gerhardt's views: ethyl iodide treated with zinc yielded a gas that Frankland identified with ethyl, C_2H_5 (according to the reaction $2C_2H_5 + Zn = ZnI_2 + C_4H_{10}$). According to Gerhardt: "Dans l'action à sec du zinc sur l'iodure d'éthyle, ce ne pas le group C_2H_5, mais lhydrocarbure C_2H_5 qui est mis en liberté, nouvel homologue du gaz des marais" (In the dry action of zinc over ethyl iodide, it is not the group C_2H_5 that is liberated, but the hydrocarbon C_4H_{10}, a new homologue of marsh gas). So, as Grimaux says (Grimaux, 1900): "The honor of discovering the synthesis of hydrocarbons of the type C_nH_{2n+2} belongs to Frankland; the honor of its interpretation belongs to Gerhardt. "

Gerhardt also came against Liebig's theory of radicals, as follows: "On one hand, radicals composed of ethyl C_4H_{10}, acetyl C_4H_6O, and benzyl $C_{14}H_{10}O_2$, join to elements reputed to be negative, such as chlorine, but they also combine with hydrogen and metals, assuming now the role of electronegative substances. On the other hand, this theory forces us to imagine an infinite number of different radicals that are all purely hypothetical compounds; ethyl, acetyl, and benzyl" (Gault, 1956).

The resounding demonstration of Laurent and Gerhardt's ideas about the nature of radical was provided in 1853 by Wurtz's discovery of mixed radicals (Wurtz, 1853a), a fact that already been predicted by Gerhardt and Gustave-Charles Bonaventure Chancel (1822-1890) (Gerhardt and Chancel, 1851): "the previous synoptic formulas indicate that in the same manner that we have a ethyl methyl ether, it is possible to obtain mixed radicals, ethyl-methyl, amyl-ethyl ether, etc."

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

5. The theory of types

During the eighteenth century the vegetable and the animal subjects 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. To these branches was added physiological chemistry, which, in France, Wurtz converted into biological chemistry in 1874 with the creation of a specific laboratory of *chimie biologique* at the Faculty of Medicine (Carneiro, 1993).

In 1813 Berzelius had proposed a classification of matter according to behaviour in electrolysis. The two major categories were imponderable and ponderable. Imponderable included phenomena such as positive and negative electricity, light, caloric and magnetism. Ponderable substances were first divided into simple and composite substances and then into two classes, electropositive and electronegative, according to whether during electrolysis they appeared at the negative or positive pole, respectively. All substances could then be arranged in the order of their electrical nature, forming an electrochemical system that could be used to give an idea of chemistry. According to Berzelius "each chemical combination should be composed of two parts united by the effect of their electrochemical reactioneach compound may be divided into two parts, of which one is electrically positive and the other negative," since only between oppositely charged elements was there attraction. Reactions occurred as the stable groups of atoms (*radicals*) were exchanged between molecules and radicals were almost as indivisible and untouchable as the individual atoms themselves (Berzelius, 1819).

To make this notion fit organic substances, Berzelius had to insist that radicals consisted of carbon and hydrogen only, with carbon negative and hydrogen positive.

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. 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, 1837).

Gerhardt put forward his theory of types, de-rived from the defunct theory of nuclei, proposed by Laurent (Laurent, 1837). Organic molecules were now grouped into families or types (*theory of 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 formic acid and stearic acid. These types were:

Water	H_2O
Hydrogen	H_2
Hydrogen chlorhydride	HCl
Ammonia	NH_3

In particular, types came in four varieties: (a) *the hydrogen type*, $\begin{bmatrix} H \\ H \end{bmatrix}$. Substitution of one or both hydrogen atoms by simple or composite radicals led to simple monatomic substances, to radicals of the same atomicity, which could be isolated, and simple or composite diatomic radicals; (b) The *hydrogen chloride type*, $\begin{bmatrix} Cl \\ H \end{bmatrix}$. To this type belonged all the compounds formed by the combination of bromine, chlorine, iodine, and fluorine, with any monatomic radical. Although this type was redundant because it could be incorporated into the hydrogen one, it was kept for reasons of commodity, (c) the *water type*, $\begin{bmatrix} H \\ H \end{bmatrix} \theta$. This group included the compounds formed by oxygen, sulfur, tellurium, and selenium (marked θ) with different monatomic radicals, and partly, those they could form with diatomic radicals. This was the interpretation given to potassium hydroxide $\begin{bmatrix} K \\ H \end{bmatrix} O$, sodium hypochlorite $\begin{bmatrix} Na \\ Cl \end{bmatrix} O$, etc., and (d) the *ammonia type*, $\begin{bmatrix} H \\ H \\ H \end{bmatrix} N$. To this group belonged ammonia derivatives or the compounds in which the nitrogen of ammonia had been replaced by phosphorus, arsenic, antimony, or bismuth (Wisniak, 2005).

A first generalization of the theory of types was admission of the possibility of substituting the hydrogen atoms of the types of water by radicals, that is, groups of atoms that were transported unchanged from one molecule to another. Thus types gave birth to acids, alcohols, ethers, hydrides, radicals, organic chlorides, ketones, and alkalis. Contrary to Liebig's, Gerhardt's radicals had no need to be able to be isolated, or of having an autonomous existence. Thus the formula for alcohol was $\begin{bmatrix} C_2 H_5 \\ H \end{bmatrix} O$, the same as that of ether $\begin{bmatrix} C_2 H_5 \\ C_2 H_5 \end{bmatrix} O$, after Alexander Williamson's sensational results (Wisniak, 2005).

The term types was not new in science; Dumas had used it to indicate that certain different sub-stances constituted the same molecular building, thus acetic acid and chloroacetic acid belonged to the same type, in opposition to the dualistic views of Berzelius. It was also, under another name, the nuclear theory of Laurent. The significant difference was that Gerhardt's theory of types embraced all of organic chemistry.

Since the above types could not help representing certain compounds which contained polyatomic radicals, Gerhardt created the simple and mixed *condensed types*, which were actually composed of the above four basic types duplicated, tripled, etc.; for example, condensed hydrogen, $\begin{bmatrix} H^n \\ H^n \end{bmatrix}$, condensed hydrogen chlorhydride, $\begin{bmatrix} C^q \\ H^{2n} \end{bmatrix} O$, condensed water, $\begin{bmatrix} H^n \\ H^n \end{bmatrix} O^n$, and condensed ammonia, $\begin{bmatrix} H^n \\ H^n \\ H^n \end{bmatrix} N^n$.

August Wilhelm Hofmann (1818-1892) (Hofmann, 1849) showed that the amines could be subsumed under ammonia as an all-embracing type: $\begin{bmatrix} H \\ H \\ H \end{bmatrix} N$ and $\begin{bmatrix} R \\ R' \\ R'' \end{bmatrix} N$, which included primary, secondary, and tertiary amines. This important finding was strongly reinforced by Williamson's discovery in 1851 of the synthesis of ethers, which allowed proving the existence of mixed ethers, R-O-R'. According to Williamson "alcohol is therefore water in which half the hydrogen is replaced by carburetted hydrogen, and ether is water in which both atoms of hydrogen are replaced by carburetted hydrogen" (Williamson, 1850, 1854). Ethers could thus be built about the water type. Inherent in Williamson's proposal was that water is H_2O and not OH, as had been maintained by many of his contemporaries, and that alcohol is not hydrated ether from which water has been removed by the action of the acid. According to the water type theory, acetic acid could be written as.

In 1852 Gerhardt applied Williamson's asymmetric synthesis to the preparation of various organic acid anhydrides, particularly acetic anhydride by the

reaction of acetyl chloride with sodium acetate (Gerhardt and Chiozza, 1853a). Williamson had produced novel asymmetric ethyl methyl ether by double decomposition between an alkali metal compound and an organic halide, and now Gerhardt produced a novel asymmetric acetic-benzoic anhydride by the double decomposition between an alkali metal compound and an organic halide. After his short reports to the Académie, Gerhardt prepared a major article for the *Annales de Chimie* (Gerhardt, 285, 1853). The committee appointed to evaluate his findings consisted of Dumas, Victor Regnault (1810-1878), and Théophile-Jules Pelouze (1807-1867). The report praised Gerhardt's chemical discoveries and agreed that his reasoning was sound and his conclusions compelling (Dumas, *et al.*, 1853).

Very important from the viewpoint of the general ideas, Gerhardt and Chiozza's memoir (1853b), about the nature of amides. The authors described a large number of new chemical species (e.g., dibenzanilide, benzoyl salicylamide, cumyl salicylamide, etc.). One of the conclusions of this work was the attachment of amides to the ammonia type, like the amines prepared by Wurtz (Wurtz, 1849) and Hofmann (Hofmann, 1849); with the difference that now the hydrogen had been replaced by acid groups instead of hydrocarbon groups. From this research also came the concept that amides were to acids what compound ammonia were to alcohols: "if we call monobasic acid a water molecule in which the hydrogen atom has been replaced by a negative radical, we shall say that the amide corresponds to the neutral salt of such an acid represented by an ammonia molecule in which the hydrogen atom has been replaced by the same negative radical, acetyl, benzoyl, sulfophenyl, etc. Amides of this sort (primary amides) have been produced thus far by the action of heat on the neutral salt, by the reaction between ammonia and the neutral ether, or by the reaction of ammonia and the corresponding acid chloride. Our experiences show that monobasic acids are also capable of yielding the amides corresponding to acid salts; in fact, our secondary amides correspond to bi-salts and our ternary amides to tri-salts. In these two classes of amides two or three hydrogen atoms of the ammonia molecules are replaced by the same negative radical or by different negative negative radicals."

In a following work (Wurtz, 1853a,b, 1854) Würtz studied the action of acids on alkyl isocyanates and discovered the substituted amides, presenting a double function: acid and alcohol, a result that complemented a previous discovery by Gerhardt and Chiozza about amides containing many acid groups (Gerhardt and Chiozza, 1853b). Wurtz applied to this series of compounds Gerhardt's views relative to acids: amides could be looked upon as acids in which one molecule of oxygen had been replaced by the residue AzH (NH) of ammonia , which had lost two hydrogen atoms, or by this same residue containing a radical that had substituted one hydrogen atom.

Wurtz had no hesitation in aligning himself with Laurent and Gerhardt; he was the first teacher in France to champion their ideas, and became the architect of a new chemical system that embraced their antidualist concepts as well as the emerging concepts of atomicity (valence) and chemical types.

The theory of types gained in popularity because it could be used to organize the rapidly proliferating numbers of organic compounds being studied. Beilstein published a vast compendium of organic compounds in 1880 and utilized Laurent's theory of types to organize those compounds into a rational order. The type concept became more general with the synthesis of many new organometallic compounds by Frankland. Now it became clear that each metallic atom would attach to itself only to so many organic groupings and that this number was different for different metals. In 1852, Frankland proposed what later would become the theory of valence (from a Latin word for "power"), which is the statement that each atom has a fixed combining power. In addition to its basic concepts, this theory helped to clarify the difference between atomic weight and equivalent weight of an element, as well between valence and oxidation number (Frankland, 1852). By 1900, the description of molecular structure in three dimensions had become universally accepted. ◤

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