

Political and Science Revolutionary

Stanislao Cannizzaro

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Resumen

Stanislao Cannizzaro (1826-1910) vivió durante el período revolucionario que llevó a la unificación de Italia. Fue partidario de Garibaldi y como tal participó activamente en los sucesos políticos y militares, al mismo tiempo que desarrollaba su carrera científica y académica. La mayor parte de su trabajo en química fue en el área de los compuestos orgánicos; a él le debemos el descubrimiento de la reacción que lleva su nombre: la reducción-oxidación de aldehídos. Su famoso *Sunto* llevó a la comprensión clara de los conceptos de átomo, molécula y peso equivalente, así como a la aceptación de la hipótesis de Avogadro. Cannizzaro demostró cómo se podían determinar los pesos atómicos a través de los calores específicos y/o la densidad de los vapores, y también que la química orgánica e inorgánica se regían por las mismas reglas. Destacó que dado que los pesos atómicos eran relativos, bastaba con elegir un peso estándar para calcular todos los otros. Su contribución a los pesos atómicos verdaderos permitió a Meyer y Mendeleev formular la tabla periódica.

Abstract

Stanislao Cannizzaro (1826-1910) lived in the revolutionary period that led to the unification of Italy. He supported Garibaldi and participated actively in the political and military events, at the same time that he was involved in his scientific and academic activities. Most of his chemical work was in the field of aromatic compounds and to him we owe the discovery of the reaction that carries his name, namely the reduction-oxidation of aldehydes. His famous *Sunto* led to a clear understanding of the concepts of atom, molecule, and equivalent weight, and to the acceptance of Avogadro's hypothesis. Cannizzaro showed

how atomic weights could be determined from the specific heats and/or vapor densities, and that inorganic and organic chemistry operated under the same rules. He stressed that since all atomic weights are relative, one standard weight had to be chosen with which all other values could be compared. His contribution on the true atomic weights permitted Meyer and Mendeleev to formulate the periodic law.

Life and career

Stanislao Cannizzaro was born July 13, 1826 in Palermo, the youngest of the ten children of Mariano Cannizzaro and Anna di Benedetto. There were six daughters and four sons. His father, born in Messina, was a magistrate who in 1826 was Direttore Generale della Polizia di Sicilia and in 1827 was elected Presidente della Gran Corte dei Conti di Sicilia; his mother came from a family of Sicilian noblemen. At the time of Stanislao's birth Sicily was under the rule of the Bourbon King of Naples and the Cannizzaro family supported the regime. Three brothers of his mother were later killed in the campaigns of Giuseppe Garibaldi (1807-1882) for the liberation and unity of Italy, two on the barricades of Palermo, in 1860, and the third at Mentana, in 1867. Cannizzaro himself became a strong anti monarchist.

His initial education was at home and in 1836, after the death of his father, he entered the boarding school Reale Collegio-Convitto "Carolino Calasanzio" where he won prizes with distinction, especially in mathematics. This early education was essentially classical although it included some mathematics. At the time of Cannizzaro's youth the school curriculum in Sicily and in the whole of Southern Italy was entirely under the control of priests. Education, "frowned on as a design of the Liberals to revolutionize the State was so successfully discouraged that in 1837 it was calculated the 2 percent of the rural population could read, and not very much of the dwellers in the towns." The teaching subjects were confined to the classical languages, grammar, and rhetoric, with very little mathematics (Tilden, 1912).

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His secondary studies were temporarily suspended during the cholera epidemics of 1837 in which he lost two of his brothers. He was also infected and after a long convalescence he returned to the boarding school and pursued courses on grammar, rhetoric, philosophy, humanities, geography, French, Latin, but no sciences. In a public contest that took place at his school in 1840 he obtained the gold medal, together with Salemi, a classmate. The justification for the prize, published on September 1840, read: “che i due allievi di rettorica, Salemi e Cannizzaro, si mostrarono non solo bene addottrinati nella letteratura latina ed italiana, spiccando il Salemi per vigore di immaginazione, il Cannizzaro per maturità di concetti. È anche di quest’ultimo notata la perizia nell’aritmetica, superiore a tutti gli altri allievi della stessa classe” (the two students of rhetoric, Salemi and Cannizzaro, showed not only to be well versed in Latin and Italian literature but Salemi outstood by his vigor and imagination and Cannizzaro by the maturity of his concepts and mathematical skillfulness above all his class mates).

In 1841, at the age of fifteen, Cannizzaro matriculated at the Faculty of Medicine of the University of Palermo. In those years the University had a very limited scope, granting degrees only in the faculties of medicine, law, and theology. During 1841-1842 Cannizzaro followed a wide variety of courses, among them literature and mathematics, although in the end he took his examinations only at the medical school. At Palermo he met the physiologist Michele Foderà (1792-1848), who introduced him to biological research. With Foderà he attempted to work out a distinction between centrifugal and centripetal nerves. In the course of this work Cannizzaro became aware of his limited knowledge of chemistry, which was very poorly taught at the University (Marotta, 1939).

In 1845 he moved to Naples where his sister Angelina had married the Marquis Ruffo, son of King Ferdinand’s II of Bourbon (1810-1859) Prime Minister, and become a lady-in-waiting of the Queen. While in Naples Cannizzaro participated in the Seventh Congress of Italian Scientists and reported the results of his physiological studies (Cannizzaro, 1845a,b). According to Marotta (1939) Cannizzaro’s talk was a dogmatic dissertation on a difficult and complex subject, the possibility of distinguishing between centrifugal and the centripetal nerves. The line of argumentation was based on experimental data and interpretations of the greatest physiologists

of the period, in addition to numerous experiments performed by Foderà and Cannizzaro. From his experiments Cannizzaro had instinctively understood that physiological processes were based on motives and now desired to pursue the study of chemistry.

At the Naples Congress Cannizzaro was fortunate to make the acquaintance of the physicist Macedonio Melloni (1798-1854), who afterwards employed him in his laboratory for a short time. Melloni was instrumental in introducing Cannizzaro to Raffaele Piria (1813-1865), professor of chemistry at the University of Pisa and the leading Italian chemist of the day, known for his work on salicin. Piria took Cannizzaro as his laboratory assistant, *preparatore straordinario*, not only teaching him chemistry but also allowing him to take part in his investigations of natural substances. At that time, Piria was just at the height of his fame, having discovered the constitution of salicin. Piria’s teachings and guidance were decisive for convincing Cannizzaro that his future laid in chemistry (Tilden, 1912).

Of his stay at Pisa, Cannizzaro wrote: “per i due anni scolastici 45-46 e 46-47. In questi due anni scolastici ebbi la mia intera educazione chimica, colla sola eccezione delle vacanze che passai in Sicilia. Il più delle volte io facevo da semplice testimone, osservando con attenzione ed in silenzio quello insuperabile modello d’ordine, di precisione e di eleganza che era il Piria nell’esperimentare e nell’analizzare” (During these two academic years, 1845/6 and 1846/7, except for a vacation in Sicily, I received all my chemical education. Most of the time I was a mere bystander watching with concentration and silence the orderly procedure, precision and adroitness that was Piria in experimentation and analysis) (Marotta, 1939).

While at Pisa Cannizzaro became a close friend of Cesare Bertagnini (1827-1857), a very promising pupil of Piria’s. Although Bertagnini died at thirty, he and Cannizzaro, along with Piria, were influential in founding an Italian school of chemistry during the early 1850’s.

In the summer of 1847 Cannizzaro returned to Palermo, intending to resume his studies at Pisa in the autumn. Once again the political events took charge. Cannizzaro found that a revolution against the Bourbons was in preparation, and in spite of the conservatism of his family, he joined the revolutionaries. In those days the political situation in Sicily was tragic. It had become a province of the Kingdom of

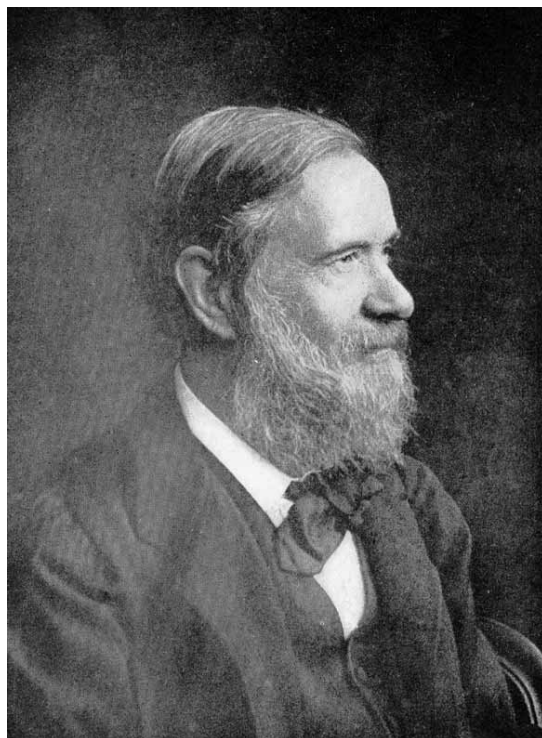


Figure 1. Stanislaio Cannizzaro (1826-1910). By permission of Edgar Fahs Smith Collection, University of Pennsylvania Library.

Naples, which the treaty of Vienna in 1815 had reconstituted for the hated Bourbon dynasty (Marotta, 1939). In January 1848 the Bourbons were driven from Naples and the kingdom of Sicily was established.

Upon the outbreak of the Sicilian revolution in 1848 Cannizzaro received a commission as an office of artillery of the new Sicilian state and took an active part in the fighting. Eventually, being only twenty-two years old, he was elected as representative of Francavilla in the so-called *Camera dei Comuni* (Chamber of Commons). After the fall of Messina he was sent to Taormina with a government commission to oppose the advance of the Neapolitan troops under the General Principe Carlo Filangeri (1787-1867), but after March 1849, the defeat at Novara, and the abdication of Charles Albert (1798-1849, the Sicilians were obliged to retreat towards Palermo (Tilden, 1912). When the insurgency failed in April 1849 he was forced into exile because his name was included in the list of those barred from returning to the Royal kingdom. On April 23, 1849, he boarded the frigate *Indipendente* for Marseille and from there he went to Paris, where, through the influence of Piria, he met Auguste Cahours (1813-

1891), who introduced him into Michel Eugène Chevreul's (1786-1889) laboratory in the *Jardin des Plantes* (today, the *Muséum d'Histoire Naturelle*). Here he resumed his chemical studies, working with François Stanislaus Cloëz (1817-1883) on cyanamide and its derivatives, and on the action of heat on cyanamide, and the polymerization induced by it. The main result of this collaboration was a paper published in 1851 describing the action of cyanogen chloride on amides (Cannizzaro and Cloëz, 1851). Cannizzaro remained in Chevreul's laboratory until 1851.

While in Paris Cannizzaro attended the lectures of Victor Regnault (1810-1878), who was at that time carrying investigations on the specific heat of the elements (Regnault, 1840). The knowledge acquired was critical in the analysis of the structure of matter that he would later describe in his *Sunto*. Regnault's influence on Cannizzaro was very strong and lasted through out his whole career.

At the close of 1851 he was able to return to Italy after being offered a position of professor of physics, chemistry, and mechanics at the *Collegio Nazionale* in Alessandria, Piedmont, where he had the advantage of a small laboratory and the services of an assistant, "un farmacista giovane intelligente" (letter to Bertagnini). Although the facilities were poor Piria urged him to accept the position because it could, and indeed did, lead to better appointments: "Io vi essorto ad accettare perchè, sebbene non si tratti che di una posizione mediocre, potreste per l'avvenire ottenere una cattedra a Torino o a Genova" (I urge you to accept, because while it is only a mediocre position, you could later on obtain a chair at Turin or Genova (Marotta, 1939). The authorities at Alessandria extended to him a grand reception; eventually a proclamation was published inviting "workers and students to hasten to the lectures to be given by our hero."

Cannizzaro now was full of enthusiasm and wrote to Bertagnini to order an elaborate list of apparatus: "Il laboratorio è in azione: è il pù poetico di tutta Italia" (The laboratory is in operation: it is the most poetic laboratory in all of Italy) (Marotta, 1939). Cannizzaro built up the research laboratory and carried out some of his best work in organic chemistry there, for example, the discovery in 1853 that aromatic aldehydes are decomposed by alcoholic potassium hydroxide in the corresponding acid and alcohol (for instance, benzaldehyde decomposes into benzoic acid and benzyl alcohol), a reaction

known today as the Cannizzaro reaction. (Cannizzaro, 1853), which he continued to study during several succeeding years (Cannizzaro, 1855a,b,c; Tilden, 1912).

The summer holiday of 1852 was spent with Bertagnini, who had a small private laboratory at Montigniso, and here they carried out work on anisic alcohol, which, however, was not published until 1856 (Cannizzaro and Bertagnini, 1856).

In 1854 Piria, in association with Carlo Matteucci (1811-1868), published the first volume of the new journal *Il Nuovo Cimento, Giornale di Fisica, di Chimica e Scienze Affini*, which became the scientific publication of the Pisan school. This journal was not established without some suspicion on the part of the Censor the Chancellor Cardinal Archbishop, "that chemistry and physics, *science periculose*, might cause some damage to the faith" (Tilden, 1912).

In 1855, as a result of his work at Alessandria, Cannizzaro was appointed professor of chemistry at the University of Genoa at the same time that Piria transferred to Turin and Bertagnini was appointed to replace him at Pisa (Tilden, 1912). During his stay at Genoa Cannizzaro wrote the letter (*Sunto*) that would later catapult him into international fame.

Once again political events changed the course of Cannizzaro's career. In the spring of 1860, the discontent of Southern Italy, responding to the unhappy events in the North, reflected in the insurrection, which erupted in April of that year. This uprising was not successful; it was crushed almost immediately by Neapolitan Royalist troops. However, on May 11 Garibaldi with his famous thousand succeeded in landing at Marsala in Sicily, and in the end forced his way into Palermo. As soon as Garibaldi had entered Palermo, Cannizzaro started for Sicily with the second expedition under General Giacomo Medici (1817-1888), although he took no part in any battle (Tilden, 1912).

In 1860 he attended the Karlsruhe Congress, at which he made known his ideas to the chemical world. The *Sunto* and the Karlsruhe congress introduced him to the scientific world, and the Italian universities began to compete with each other for him.

In October of 1861 Cannizzaro returned to Palermo to take part in the new government as member of the Extraordinary Council of the State of Sicily and as professor of inorganic and organic chemistry at the University. Eventually he became Rector of the University.

In Palermo he took part in many political and educational activities: he became a member of the Municipal Council, a position he used to secure the establishment of schools, which were almost entirely wanting, as well as to provide for the higher education of women. In 1867 he acted as Commissioner of Public Health during one of the outbreaks of cholera, in the course of which he lost a sister, struck down by the disease while nursing the sick (Tilden, 1912).

In 1863 he gave the inaugural speech of the academic year, entitled *La Chimica e le Scienze Naturali*, where he exposed the philosophy that governed his thinking (Marotta, 1939). Cannizzaro stayed in Palermo for ten years and during this time he did considerable research on the derivatives of benzyl alcohol and other aromatic compounds (Tilden, 1912). Once more he had to organize and build a laboratory since the only facility available for chemical research was the same small room that had been available in his student days. Cannizzaro was so successful in his efforts that Palermo became the center of chemical education in Italy and brought to his laboratory Italians as well as foreigners anxious to learn. Wilhelm Körner (1839-1925), who devised the method of locating the position of substituents in the benzene ring, Adolf Lieben (1836-1914), later a noted organic chemist in Vienna, Alfred Naquet (1834-1916), and Emanuele Paternò (1847-1936) were among his students. The names of Cannizzaro and Körner are associated together in the authorship of a paper on anisic alcohol (Cannizzaro and Körner, 1872; Tilden, 1912; Marotta, 1939).

In 1871, with the reunification of Italy, Cannizzaro made his last move to Rome as senator of the Kingdom (subsequently he became Vice-President of the institution) and as first in the new chair of chemistry at the University of Rome, which he retained until his death. While in Rome he transformed the old Convent of San Lorenzo (in Panisperna) into the first Italian Institute of Chemistry and started his work on monobenzil urea and other researches that constituted the continuation and the conclusion of his previous chemical activities. With only the use of primitive means available at that time, Cannizzaro worked out the constitution of santonin in collaboration with Amato (1874), Carnelutti (1877), Sestini (1875), Valente (1876), Gucci (1892), and others. Cannizzaro spent in Rome the remainder of a long and brilliant career and under his inspirations many of the greatest Italian scientists received their training (Tilden, 1912).

As a moderate liberal he played his part in shaping the Constitution and establishing reform in the affairs of the now united Italy. Among his public activities were the organization of the Laboratorio Chimico de la Gabelle (the chemical laboratory of Customs) and the State Regia dei Tabacchi. He was also a member of the higher Council of Public Education, of which some time he was President. He further occupied himself with provision of public instruction in agriculture, and generally in helping forward the advancement of science and the liberal professions in Italy. When the Congress of Applied Chemistry met in Rome in 1906, Cannizzaro was elected Honorary President (Tilden, 1912).

On September 24, 1857, Cannizzaro married, in Florence, Harriet Withers, the daughter of the Reverend Edward Withers, of Marlstone, Berkshire. The ceremony took place at the British consulate because Enricheta (as Cannizzaro called her in his letters) was Protestant. They had one son (Mariano, born in 1858, who became an architect) and a daughter (Ana, born in 1860).

Cannizzaro died in Roma, May 10, 1910 at the age of 84 years. On the centenary of his birth in 1926, during the Second National Italian Congress of Pure and Applied Chemistry, his body was transferred to the Pantheon at Palermo.

Cannizzaro is best known for the reaction that carries his name and for his *Sunto di un Corso di Filosofia Chimica* (Sketch of a Course in Chemical Philosophy), published in 1858 and widely publicized in 1860 at the Karlsruhe Conference. As explained below, this document was instrumental in establishing the concepts of atom, molecule, equivalent, and atomic weights, and on the manner to determine the atomic weights of the elements in volatile compounds from the molecular weights of those compounds or from knowledge of their specific heat. For this achievement of fundamental importance for the atomic theory of chemistry the Royal Society awarded him the Copley medal in 1891.

Cannizzaro was a foreign member of the American Chemical Society and of the German Chemical Society. On June 19, 1862, he was also elected foreign member of the Chemical Society of London; he was the second Faraday lecturer of the Chemical Society (1872) and the subject of the address he gave then was "The Limits and Form of Theoretical Instruction in Chemistry."

In 1894 the Académie des Sciences elected Can-

nizzaro as *Correspondant*, replacing Jean Charles de Marignac (1817-1894) that had passed away.

Scientific achievements

Cannizzaro published about 80 papers, 56 in organic chemistry, 12 theoretical, 4 physical, 5 biographical, 2 educational, and 4 miscellaneous. Most of his work in organic chemistry was devoted to the reactions and structure of *santonin*.

According to Tilden (1912) the main contributions of Cannizzaro may be summarized as follows: (a) He established in a definite way the two principal methods by which atomic weights can be determined: one by reference to the molecular weights derived from the application of Avogadro's principle, and the other using Dulong and Petit's relation between atomic weight and specific heat of the solid elements (Petit and Dulong, 1819). He also demonstrated the equivalence of both methods, and, (b) He unified organic and inorganic chemistry showing that the same principles apply to both.

1. Organic chemistry

Cannizzaro carried out all of his experimental work in the field of organic chemistry, particularly on the preparation and properties of aromatic alcohols (Cannizzaro, 1860a,b, 1862). In 1853, while studying the behavior of benzaldehyde, he discovered its reaction with potassium hydroxide, in which an oxidation-reduction produces both benzoic acid and benzyl alcohol (the Cannizzaro reaction, 1853, 1854). Among other things he proposed giving the name hydroxyl to the -OH group, and he defined the reactions of the alcoholic, phenolic, and acidic *ossidriles*. His efforts during the latter part of his life were devoted to determining the structure of *santonin* (C₁₅H₁₈O₃, obtained from the flowers of *artemisa* and used as a vermifuge), which he showed to be one of the few natural compounds derived from naphthalene. Cannizzaro recognized that *santonin* behaves like a ketone and may be reduced to a secondary alcohol and an oxime. He used *santonin* to synthesize dimethylnaphthalin, dimethylnaphthol, and propylene.

Together with Bertagnini he studied anisic alcohol and converted benzyl chloride into phenylacetic acid (Cannizzaro and Bertagnini, 1856).

2. Sunto

Cannizzaro's lasting fame is the outcome of a letter he wrote in 1858 to his friend Sebastiano de Luca

(1820-1880), who had succeeded Bertagnini in Piria's chair at Pisa. This was the famous *Sunto di un Corso di Filosofia Chimica fatto nella Reale Università di Genova*, published in the journal *Nuovo Cimento* (Cannizzaro, 1858) and reprinted as a pamphlet in Pisa, 1859.

To understand the significance of this document it is important to understand the state of the knowledge regarding some basic concepts such as atoms, molecules, and equivalents, which were prevalent in the mid 1860s. When Cannizzaro wrote the *Sunto*, there was no agreement among chemists as to what values should be adopted for atomic, molecular, or equivalent weights; no possibility of systematizing the relationship of the various elements, and no unanimity as to how organic compounds should be formulated.

According to Dalton (Dalton, 1808) gases are formed by particles of roughly globular form and kept apart by virtue of the fact that each individual atom surrounded itself by an appropriate measure of caloric. Since different gases had different affinities of caloric, their particles had to have different sizes and, therefore, they must be in different numbers in a given volume, thus rejecting Joseph-Louis Gay-Lussac's (1778-1850) hypothesis on the simple ratios of combining gases (Gay-Lussac, 1809). Dalton saw weight as the fundamental parameter. He applied this concept to Antoine-Laurent Lavoisier's (1743-1794) elements, which he supposed to consist of atoms. The existence of such atoms was encouraged in his mind by his being able to conceive a mechanical model of them, like lead shot. In his *New System of Chemical Philosophy* (1808) Dalton wrote: "Upon reconsidering this subject, it occurred to me that I had never contemplated the effect of a difference in size in the particles of elastic fluids... The different sizes of the particles of elastic fluids under the circumstances of temperature and pressure once established, it became an object to determine the relative sizes and weights, together with the relative number of atoms in a given volume. This led the way to the combinations of gases and the number of atoms entering into such combinations... Thus a train of investigations was laid for determining the number and weight of all chemical elementary principles which enter into any sort of combination one with another." Dalton's book contains the first published table of the relative weights of the ultimate particles of gaseous and other bodies, calculated from the analysis of compounds by the aid of certain hypothesis. From the composition of water and ammonia he

deduced the atomic weight of oxygen as seven and of nitrogen as five, assuming hydrogen as unity, and he confirmed these values by examining the nitrogen oxides.

Dalton proposed that the elements are composed of atoms that are indestructible, that atoms of different elements differ in their masses, and that a compound is a characteristic grouping of atoms. He considered the law of definite proportions a postulate and he expressed the law of multiple proportions as a corollary to it: When two elements combine in a series of compounds, the ratios of the masses of one element that combine with a fixed mass of the second are reducible to small whole numbers. On the basis of these postulates Dalton tried to calculate the masses (molecular weights) of well-known compounds like water, ammonia, NO, and NO₂, making the faulty assumption that the molecules of an element are always *single atoms*, and thus hydrogen and oxygen would combine to form HO (instead of H₂O).

Dalton's hypothesis and first determination of the relative weight of atoms were followed by many attempts to establish the value of the relative, if not the absolute weights of atoms. Considerable advances were made in this direction, notably by Jöns Jacob Berzelius (1779-1848), Jean-Baptiste André Dumas (1800-1884), Théophile-Jules Pelouze (1807-1867), Jean Charles de Marignac (1817-1894), and Jean Servais Stas (1813-1891). Nevertheless, the numerical results afforded by experiment were only equivalents or combining proportions, uncorrected by reference to any standard.

Up to the second half of the eighteenth century the idea that the ultimate particles of the elements themselves might contain more than one atom had not been commonly accepted. It was believed that combination could only occur between substances of opposite chemical or electrochemical character, hydrogen with oxygen for instance, but that hydrogen could unite with hydrogen or oxygen with oxygen, was not generally admitted (Tilden, 1912). Dalton expressed his belief that "We might as well attempt to introduce of new planet into the solar system, or to annihilate one already in existence, as to create or destroy a particle of hydrogen. All the changes we can produce, consist in separating particles that are in a state of cohesion or combination, and joining those that were previously at a distance."

Gay-Lussac extended the relationship between chemical masses implied by Dalton to the volumetric

relationships of gases. In 1809 he published two observations about gases that have come to be known as Gay-Lussac's laws of combining gases (Gay-Lussac, 1809): (a) When gases combine chemically, they do so in numerically simple volume ratios and, (b) If gases combine to form gases, the volumes of the products are also in simple numerical ratios to the volume of the original gases. Gay-Lussac illustrated the last statement by the combination of carbon monoxide and oxygen to form carbon dioxide and claimed that the volume of the carbon dioxide produced is equal to the volume of carbon monoxide and is twice the volume of the required oxygen. In doing so, he repeated the mistake of Dalton in not considering that the reason why only half as much oxygen is needed is that the oxygen molecule splits in two to give a single atom to each molecule of carbon monoxide.

Gay-Lussac's memoir on combining volumes was central to the formulation of the molecular hypothesis. According to Thomson (Thomson, 1813) "The object of Gay-Lussac paper was to confirm and establish the new atomic theory, by exhibiting in a new point of view... We only have to consider a volume of gas to represent an atom, and then we see that in gases one atom of one gas combines either with one, two, or three atoms of another gas, and never with more."

According to Berzelius's dualistic theory "each chemical combination should be composed of two parts united by the effect of their electrochemical reaction... each compound may be divided into two parts, of which one is electrically positive and the other negative," since only between oppositely charged elements there was 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). Although Berzelius concurred with the idea that equal volumes of gases contain an equal number of atoms, he established a clear distinction between simple and compound gases. He admitted that equal volumes of the first contained an equal number of atoms, but denied all significance to the ratio between the volumes of compounds and their elements. The radical hypothesis presented some difficulties in interpreting known phenomena. For example, how was it possible to explain that two hydrogen atoms could unit to become a hydrogen molecule? Attraction between two atoms required that one of them be positive and

the other negative, but why should two atoms of the same kind possess charges with opposite charges? Thus Berzelius was led to the impossibility of admitting that the molecules of elements could contain more than one atom because it would imply the union of two radicals of the same charge. When the knowledge of organic compounds increased, new difficulties arose. Berzelius, for example, found it necessary to assume that the hydrogen atom was always positive and the chlorine atom always negative.

Another fundamental factor in Berzelius' system was the use of oxygen not only as standard of atomic weights (assuming O = 100) but also of combining capacities. This criterion led him to assume that ammonia, in opposition with the ratio between the volumes of the components, had the double formula N_2H_6 , which represented the amount of base which combined with a compound atom of water (containing one atom of oxygen) in order to produce oxy-salts (sulfate, etc.) (Parravano, 1927).

With increased knowledge, problems that could not be explained by Berzelius's theory became increasingly numerous and the theory became discredited. By the end of the nineteenth century it had become obvious that the only way to explain certain phenomena was to accept that there were different kinds of chemical bonds; thus the difficulties of Berzelius's theory were also explained.

In 1811 Amedeo Avogadro (1776-1856) published an article in *Journal de Physique* where he analyzed the laws of Gay-Lussac and Dalton's position with respect to the structure of the elements (Avogadro, 1811). In the opening paragraph he claimed that Gay-Lussac laws implied that very simple relations also existed between the volumes of gaseous substances and the number of simple or compound molecules that formed them. Not only that, he advanced that the only admissible hypothesis was that *the number of integral molecules of any gas contained in a given volume is always the same for equal volumes, or always proportional to the volumes*. In addition he clearly drew the distinction between molecule and atom and pointed out that Dalton had confused both concepts. The "atoms" of nitrogen and oxygen were actually "molecules" containing two atoms each. Thus two molecules of hydrogen could combine with one molecule of oxygen to produce two molecules of water. Avogadro illustrated the difference between his approach and that of Dalton by saying that since Dalton assumed that water was formed by

the union of one molecule of hydrogen with one molecule of oxygen, then from the ratio by weight of the two components it followed that the mass of the molecule of oxygen to that of hydrogen would be as $15/2 : 1$ or, according to Dalton, as 6:1. According to Avogadro's hypothesis the actual ratio should be *twice* as great, namely as 15:1. Hence the mass (molecular weight) of water should be roughly $15 + 2 = 17$.

Avogadro worked hard to prove that the apparent contradiction between Gay-Lussac's volumetric approach and Dalton's atomistic approach could be bridged. He asserted the accuracy of his approach in determining chemical composition and that it allowed assigning the mass of compound molecules according to the volumes of the gaseous compounds. He specified that his procedure depended partly on the division of molecules, "a fact unexpected by Dalton." We must mention that the idea of split molecules had been considered by others at the time but rejected because it conflicted with the widely accepted "indivisible" atomic theory of Dalton.

As mentioned above, Dalton thought of gases as formed by particles of roughly globular form, whose size was represented by a hard center surrounded by an atmosphere of caloric. A repulsive force, inversely proportional to the particles' affinity for caloric, balanced their mutual attraction. Since different gases had different affinities for caloric their particles had to have different sizes and therefore, they must be in different numbers in a given volume. Avogadro contested these ideas by saying that if they were correct then it would be impossible to explain the simple ratios found in the combination of different gases reported by Gay-Lussac. A more logical answer consisted in assuming that in a gas the intermolecular distances are so large that no mutual action between such molecules could take place. Under these conditions, a change in the attraction for the caloric exhibited by each molecule might affect the amount of caloric condensing around it, but not its volume. Thus it was reasonable to assume that under equal volumes (or under equal temperature and pressure) there was always the same number of molecules.

The natural consequence of Avogadro's law of "equal volumes, equal number of particles" was that the ratio of the weights of equal volumes of gases had to be equal to *the ratio of the weights* of the single particles of each individual gas. When these gases reacted with one another, for example, if one volume

of *A* reacted with two volumes of gas *B* to yield two volumes of gas *C*, then it was obvious that one particle of *C* was formed of one particle *B* and one-half particle *A*. Acceptance of the existence of one half-particle of *A* either meant acknowledging that each particle was constituted of two atoms, or the incongruous proposition of adopting a divisible atom. The questionable point of Avogadro's law, as enunciated by him, was, therefore, the meaning of the term "particle" (Marotta, 1939).

During the years 1825-1860 the efforts of most of the outstanding chemists, Justus von Liebig (1803-1883), Friedrich Wöhler (1800-1882), Auguste Laurent (1807-1853), Charles-Frédéric Gerhardt (1816-1856), Charles-Adolph Würtz (1817-1884), Alexander Williamson (1824-1904), August Kekulé (1829-1896), Dumas, Hermann Kolbe (1818-1884), and Edward Frankland (1825-1899), were directed to the organic field, the compounds of carbon. Each of them had their own theory, some times quite different or opposite to that of another scientist. The arguments were a rich fertilizer of the ideas, which eventually would lead to a common denominator. The initial divergences were so large that, for example, in 1859 Kekulé filled a whole page of his textbook with different formulae of such a simple compound as acetic acid, and the formula of water was written in four different ways, H_2O , HO , HO , H_2O_2 (Hartley, 1971).

One of the first fundamental attempts to interpret organic reactions on similar arguments as inorganic ones was done by Laurent and Gerhardt. In 1836, Auguste Laurent (1807-1853), a student of Dumas, realized the chlorination of ethanol (Laurent, 1836). This experiment was the 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. 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. Gerhardt's system of four types: water, hydrogen chloride, ammonia, and hydrogen, was adopted by him only for the purpose of classifying reactions, as he insisted repeatedly that any knowledge of the arrangements of atoms in a compound is inaccessible by experiment. The idea of types led indirectly to the idea of linking atoms, but the time had not arrived yet when the property of atoms, which is now called valence, could be recognized (Tilden, 1912).

Gerhardt examined a large number of chemical reactions and concluded that they might be represented very simply expressing the stoichiometry in terms of gas volumes; the quantities contained in equal gaseous volumes must, therefore, be chemically comparable. In 1843 he pointed out that the equivalents accepted for organic compounds did not agree with those assigned to mineral substances, and in order that they might correspond with H_2O , CO_2 , and NH_3 , they required to be reduced to one half. At the end of a series of papers on the subject (Gerhardt, 1843a,b), he summed up his conclusions in the following sentences:

- (a) "Atomes, equivalents et volumes sont synonyms (atoms, equivalents, and volumes are synonyms),
- (b) Les densités des gaz sont proportionnelles à leurs equivalents" (the densities of gases are proportional to their equivalents).

Gerhardt took the water molecule as unity, representing it by the formula H_2O ($O = 16$), and from this he was led to represent elementary hydrogen as hydrogen hydride, HH , and gaseous chlorine as chlorine chloride, $ClCl$.

It was this confusion of ideas that stimulated Cannizzaro in 1858 to give a course of lectures to his students in which he tried to rationalize the concepts of atom and molecule and of atomic and molecular weight (Hartley, 1971). In his letter to de Luca he gave an extensive description of the first eight lectures, which in fact constitute the medulla of his exposition.

Cannizzaro's *Sunto* (Cannizzaro, 1858) begins with the following words: "I believe that the progress of science made in these last years has confirmed the hypothesis of Avogadro, of André-Marie Ampère

(1775-1831), and of Jean-Baptiste André Duma (1800-1884) on the similar constitution of substances in the gaseous state; that is, that equal volumes of these substances, whether simple or compound, contain an equal number of molecules, not, however, an equal number of atoms, since the molecules of the different substances, or those of the same substance in its different state, may contain a different number of atoms, whether of the same or different nature."

In the *first lecture* Cannizzaro gives an historical description of the development of the chemical theories of matter and shows that the hypotheses postulated by Avogadro, Ampère, and Dumas does contradict known physical facts, as long as a clear distinction is made between atoms and molecules, and as long as we accept that the *molecules of compound substances* may consist of different number of atoms, and the *molecules of simple substances* (the elements) must all contain either one atom, or at least an equal number of atoms. The non-acceptance of Avogadro's ideas was caused by the confusion that prevailed at that time between molecules and atoms.

In the *second lecture* he investigates the reasons why the hypothesis of equal volumes = equal number of particles was not immediately accepted, this being so because the different scientists did not look into the possible relationships between the quantities of substances reacting and their volumes in the gaseous state. He then explains the theories of Berzelius and how they misled him into the wrong conclusions. Berzelius developed and completed the dualistic theory of Lavoisier with his electrochemical hypothesis, but unfortunately, he assumed that atoms, which were separated in the elements, would unite to form the atoms of a compound of the first order, and these in turn would unite in simple proportion to form composite atoms of a second order. Not only that, when two molecules of a substance would unite with one molecule of another one they would generate a single compound; instead of producing *one* single molecule, they would produce *two* molecules of the same nature (thus negating Avogadro's hypothesis).

The *third lecture* reviews all the researches done from Gay-Lussac to Rudolf Julius Emanuel Clausius (1822-1888) and shows that all of them confirm Avogadro's and Ampère's hypothesis that the distance between molecules in a gas at constant pressure and temperature, is independent of their nature, their mass, and the number of atoms they contain.

The *fourth lecture* discusses first the methods developed by Berzelius and Dumas to determine the formula of organic and inorganic compounds, based on the wrong idea that there were different rules governing inorganic and organic chemistry, and then the findings of scientists like Gerhardt, Williamson, Würtz, Marcellin Berthelot (1827-1907), Frankland, and others which tried to bring both parts of chemistry into harmony. While Berzelius did not admit that the molecules of simple substances could be divided during a reaction, Gerhardt assumed that the molecules of all the elements could, an error in reasoning that led him to assume that the molecules of mercury and of all metals consist of two atoms like that of hydrogen.

In his *fifth lecture* Cannizzaro shows how Avogadro's hypothesis can be used to determine the weights of molecules, without necessarily knowing their composition. The hypothesis leads to the fact that the weights of molecules must be proportional to the densities of the substances in their gaseous state. Cannizzaro stresses that since all atomic weights are relative it is then necessary to choose one standard weight with which all other values can be compared. He chose hydrogen as this standard, but since he knows it to be diatomic, he uses *half a molecule of hydrogen* as unity. He then tabulates the atomic weight of ten substances relative to that of hydrogen assumed as 1. This table contains some interesting facts: The atomic weight of ordinary oxygen is given as 16 while that of electrified oxygen is 96 (ozone); the atomic weight of sulfur below 1000°C is 96 and above 1000°C it is 32. As stated by Cannizzaro, the table shows that the same substance in different allotropic states can have different molecular weight. He then declares: "The different quantities of the same element contained in different molecules are all multiples of one and the same quantity, which, always being entire, has the right to be called a atom" (La più piccola quantità di un elemento capace di entrare a far parte delle combinazioni, rappresenta appunto il peso atomico dell'elemento).

The *sixth lecture* is devoted to the study of the constitution of molecules of various chlorides, bromides, and iodides. Since the greater part of these compounds is volatile and the density of the gas is known, then there is no problem in determining the molecular weight of the compound and the amount of the halogen present in it. Given that the latter must always be an integral multiple of the weights of the halogen contained in the pertinent hydro acids, it is

a simple matter to calculate the number of atoms existing in the compound in question. A special point is the composition of the molecules of the two chlorides and the two iodides of mercury. Cannizzaro proceeds to show that the smallest proportion of mercury present in any molecule containing that element is 200, and this is, therefore, the atomic weight of the metal. This number is then confirmed by applying Dulong-Petit's law of specific heats to the chlorides and iodides of mercury, as well as to the specific heats of solid bromine, iodine, and solid mercury. The results indicate that the weight 200 of mercury whether as an element or in its compounds, requires the same quantity of heat as 127 of iodine, 80 of bromine and 35.5 of chlorine, and 1 of hydrogen. Next, the analogy of the chlorides of copper with those of mercury leads to the examination of these compounds, but as the vapor densities of these salts are not known, the specific heat of copper and of its compounds suggests the number 63 as the atomic weight of copper. Since the vapor density of this substance has not been determined yet, there is no way of knowing if this is the real molecular weight of the uncombined metal, or not. Many other metals (potassium, sodium, lithium, silver, gold, etc.) are then examined, and as Cannizzaro points out, for metals such as tin, which produces volatile compounds without decomposition and for which the molecular weight can be determined, the atomic weight deduced from specific heat is in agreement with those derived from vapor density. But then the question arises: "Are the atoms of these metals equal to their molecules, or to a simple sub-multiple of them?" And then he adds: "I gave you above the reasons which made me think it probable that the molecules of these metals are similar to that of mercury, but I warn you now that I do not believe my reasons to be of such value as to lead to that certainty which their vapor densities would give if we only knew them." Herein he differs from Gerhardt, who supported the view that the atoms of hydrogen, chlorine, and oxygen were half-molecules, and that the molecules of water contained twice as much hydrogen as that of hydrogen chloride, but the atoms of all the metals were like that of hydrogen a simple sub-multiple of the molecule.

In the *seventh, eighth*, and following lectures Cannizzaro studied some monatomic and diatomic radicals and what he called "their capacity of saturation". After defining diatomic radicals as "those which not being divisible, are equivalent to two of hydrogen or

to two of chlorine”, he proceeds to show “that cadyle, (tetramethyl diarsine, $C_2H_6As_2$), methyl, ethyl, and the other homologous and isologous radicals are like the atom of hydrogen, monatomic, and, like it, they cannot form a molecule alone but most associate themselves with another monatomic radical simple or compound, whether of the same or of a different kind, and that ethylene, propylene, are diatomic radicals analogous to the radicals of mercuric and cupric salts, and to those of the salts of zinc, lead, calcium magnesium, etc., and that these radicals, like the atom of mercury, can form a molecule by themselves. The analogy between the mercuric salts and those of ethylene and propylene has not been noted, so far I know, by any other chemist” (Tilden, 1912).

The *Sunto* also discusses the problems associated with the determination of the molecular weight of compounds that decompose in the vapor phase. Cannizzaro used Gerhardt and Laurent’s arguments to show that the vapor densities of organic compounds were consistent with the atomic weights determined by his method and with the value calculated with Gerhardt’s formula. An important observation was related to the fact that Gerhardt had assumed that all metallic monoxides had the same formulae as water. This fundamental mistake had led Gerhardt to assign the wrong values to the atomic weights of many metals. In addition, Cannizzaro showed that the apparent anomalies presented by the vapor densities of ammonium chloride, hydrogen sulfide, and mercuric chloride were due to their dissociation in the vapor state.

3. The Karlsruhe conference

By the middle of the 19th century the conflicting opinions on the structure of matter and the indivisibility of molecules had resulted in a chaotic situation regarding chemical notation. Berzelius and his followers, for example, used the general formula MO for the chief metallic oxides, while others assigned the formula used today, M_2O . A single formula stood for different substances, depending on the chemist: H_2O_2 was water or hydrogen peroxide; C_2H_4 was marsh gas or ethylene, and so on.

To try to solve this and other problems Kekulé early in 1860 proposed to his friend Carl Weltzien (1813-1870), professor of chemistry at the Technische Hochschule in Karlsruhe, the organization of an international meeting of chemists. Würtz also promised his support and so in March 1, 1860, the three

met in Paris to discuss the project with the French chemists, who agreed to support it. In June, a letter printed in English, French, and German, and signed by forty-five of the leading chemists in each country, was widely circulated, inviting the recipients to attend an international conference to be held at Karlsruhe on 3 to 5 September, with the main purpose of trying to reach an agreement on the following points: (a) Would it be judicious to establish a difference between the term atom and molecules? (b) Would it be judicious to designate by the term molecules the smallest quantity of a body capable of entering into combination? (c) Would it be judicious to designate by the word atom the smallest quantity of a body existing in combination? (d) Should the term compound atom be suppressed and replaced by the words residue or radical? and, (e) is the idea of equivalents empirical and independent of the idea of atom or molecule?

The organizing committee included such distinguished scientists, as Robert Wilhelm Bunsen (1811-1899), Cannizzaro, Dumas, Hermann von Fehling (1812-1885), Hermann Kopp (1817-1892), Liebig, Louis Pasteur (1822-1895), Regnault, Wöhler, and Würtz. Many of the well-established old men, such as Wöhler and Liebig, did not attend (De Milt, 1951).

At the opening session Weltzien welcomed the members and took the chair with Würtz, Henry Enfield Roscoe (1833-1915), Kekulé, Adolph Strecker (1822-1871), and L. Schischkoff as secretaries. The notes of Kekulé’s opening speech show that he failed entirely to give a clear directive to the conference. He proposed that they should appoint a committee to formulate questions for discussion by the conference on the following day. The first meeting of the committee revealed a fundamental difference of approach by Kekulé and Cannizzaro as Kekulé would accept only chemical evidence for the determination of atomic and molecular weights and would not accept Cannizzaro’s view of the identity of the physical and chemical molecule, pointing out the anomalies of the vapor densities of sulfur, ammonium chloride, and sulphuric acid. For Kekulé a chemical molecule was the smallest unit to enter into a chemical reaction while physical molecules were the ones assumed by the kinetic theory of gases (Hartley, 197).

Although Cannizzaro’s speeches before the Karlsruhe Congress were considered to have been the most eloquent: “Professor Cannizzaro, in an impromptu speech, at once remarkable both for

profundity and style, combated the ideas of M. Kekulé" (Anonymous, *Chem. News*, 186), he left at the end of the meeting probably feeling that his efforts had been wasted. However, his friend Angelo Pavesi (1830-1896), professor of Chemistry at the University of Pavia, remained behind and distributed copies of the *Sunto*, which Cannizzaro had brought with him. This was the decisive step for it brought Cannizzaro's clear and logical arguments to the attention of the chief chemists of the day. The copies distributed by Pavesi made a very strong impression on one of them: Lothar Meyer (1830-1895). In a prefatory note to the German edition of *Sunto* (published in 1891) Meyer relates how he received at the Karlsruhe meeting a copy of this paper, which he read with surprise at the clearness with which all the most important difficulties were removed. He says: "I read it again and again and I was amazed at the clear light which that little paper shed on the main subjects of our debates. The scales fell from my eyes, doubts disappeared and a feeling of certainty took their place... I owe much to Cannizzaro's pamphlet... After the apparent discrepancies between the laws of Avogadro and Dulong and Petit had been explained by Cannizzaro, both could be used to the full and thereby the doctrine underlying the chemical values of the elements was put on a sound foundation without which the theory of atomic linkages could not have progressed." (Ostwald, *Klassiker* 90).

Meyer's book *Die Modernen Theorien der Chemie* (Meyer, 1864) utilized Cannizzaro's ideas throughout and exerted a strong influence on the chemical world. Dmitri Mendeleev (1834-1907) also attended the congress and later wrote of the defence that Cannizzaro had presented for Avogadro's hypothesis (De Milt, 1951). By the end of the 1860's, when Meyer and Mendeleev had already formulated independently the periodic law of the elements, the reformed atomic weights had ceased to be controversial. By 1870 Cannizzaro's views were generally accepted, except in France. Among the most obstinate French opponents of the theory were Marcelin Berthelot (1827-1907) and Henry Sainte-Claire Deville (1818-1881). Berthelot could never agree that matter, even in the gaseous state, could obey such simple laws as those enunciated by Avogadro; Berthelot referred to it rhetorically (Berthelot, 1877): "La Note que vient de lire notre savant confrere me paraît réclamer une réponse de la part des personnes qui, comme moi, sont restées fidèles au langage des

équivalents, et oppose à la notation atomique... explications ingénieuses me semblent de simples assertions sans preuve... En réalité, nous ne voyons pas les molécules, et nous n'avons aucun moyen connu pour les compter... Il y a là deux notions hypothétiques, celle de la molécule et celle de l'atome. Qui a jamais vu, je le répète, une molécule gazeuse ou un atome" (The Note just read by our illustrious colleague needs to be answered by those, who like me, remain faithful to the language of equivalents and oppose the atomic notation... ingenious explanations that seem to me simple assertions without proof... In reality we do not voyons molecules and we do not have any known method of counting them... We have here two hypothetical notions, that of a molecules and that of an atom. Who has ever seen a gaseous molecule or an atom?). Deville's objections were based on some apparent anomalies in the behavior of matter in the gaseous state. Cannizzaro was able to show, however, that all this was due to phenomena of molecular dissociation, a subject on which Deville was well versed and interested.

According to Parravano (1927), Cannizzaro's *Sunto* represents to this day the clearest exposition of that body of doctrines, which have formed the atomic theory, until the rising of modern atomistics. ■

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