Joseph Louis Proust

Life and career1-7

Joseph Louis, the second of the three sons of Rosalie Sarthe (?-1786) and Joseph Proust (?-1792), a distinguished local pharmacist, was born in Angers, France, on September 26, 1754. His elder brother Joachim (1751-1819), apothecary apprentice, and an ambitious and strong character young man, abandoned soon the profession and joined the Regiment Infantry del Piedmont, located in Corcega. At the end of his military contract, he moved to Paris where he played an important political role during the French Revolution: member of the municipal counsel of Angers, and of the first Revolutionary Committee. In this position, he was in charge of organizing the industries of gunpowder and saltpeter. Joseph Louis’s youngest brother, François Jacques (1756-?), emigrated to Île de la Réunion and eventually became major of the city of Mauritius.1,3

Joseph Louis began his education under the care of his godparents, M. Maunoir and Rosalie de Joanneaux, a friend of his mother, and continued it at the local collège des Oratoriens (Oratorian college). Like the Jesuits, the Oratoriens were specialists in education. The secular priests of the Oratory opened many schools in Italy and France, and played an important role in the education of young people in both countries. The curriculum included Theology, Philosophy, Humanities, Physics, and afterwards Mathematics. Towards 1765, when Proust started his studies, the teaching level was in decadence, mainly because of the opposition of the Jesuits and the priests of Saint-Aubin, caused by the adhesion of the Oratorians to the Jensenian heretic doctrines. The Oratory was dissolved by the French Revolution and re-established in 1852.1,3,6

After finishing college Joseph Louis studied pharmacy in his father’s shop and in the School of Medicine and Pharmacy of Angers. Around 1774, despite the parental opposition, he went to Paris to continue his training.2,4 There he obtained a position as assistant in the well-known laboratory of the apothecary Nicolas François Cleramburg, and also took chemistry lessons under Hilaire Martin Rouelle (1718-1779) and Jacques Alexander Cesar Charles (1746-1823).1,3

In 1776, he competed and gained the position of gagnant maîtrise, pharmacien en chef, of the Hôpital de la Salpêtrière in Paris. Curiously, Proust did not postulate, some
of his friends placed his name on the list. The selection committee voted unanimously
for him. This position provided Proust with an adequate income and the means of
continuing his study of chemistry, which led to his work on pyrophore without alum and
the rapid combustion of essential oils by nitric acid, urine, and the synthesis of carbon
disulfide by the dry route, etc. All these activities translated into his first scientific
publications and also to be classified by the authorities of the hospital as a very poor
pharmacist and accused of “un emploi abusif des drogues les plus chères pour faire des
expériences de Chimie” (abusive use of very expensive materials to make his chemical
experiments). The Salpêtrière was one the major hospitals established in 1656 by a
decree of Louis XIV “to attend the poor beggars of the city and the district of Paris”.
The position of gagnants-maîtrise was regulated by the same decree: “we wish that the
apothecaries and surgeons corps provide each two of their members able to serve
gratuitously in the hospital, assisting the poor and the officers and servants of the
institution, for their common illnesses, and after a period of six years these apothecaries
and surgeons will attain their maîtrise by certifications of the directors, and be granted
the same rights and privileges as the other maîtres”.

In 1778, Proust accepted his first appointment in Spain, where he would spend the
main part of his professional life as professor of chemistry at the recently established
Real Seminario Patriótico Vascongado at Vergara, in the Basque county. This school
was the creation of the Real Sociedad Económica Vascongada de Amigos del País
(established in 1765), the first and most important of the “enlightened” provincial
societies in Spain. An elite, devoted to sciences and technology, had established the
Sociedad Vascongada in the ancient Villa Vergara to promote the advancement and
general progress of the Basque country. The King of Spain had authorized the
establishment of two chairs, one in chemistry and another in Mineralogy and
Metallurgy, which would be financed by the Crown. Hilarie Rouelle suggested hiring
Henel, one of his former students to the chemistry chair. When Henel refused to travel
to Spain, Proust, another former student of Rouelle, was approached and accepted the
position.

In June 1780, Proust went back to France and during the next five years taught
chemistry at the Musée, a private teaching institution founded by Jean-François Pilâtre
de Rozier (1754-1785) in 1781. Proust collaborated with his friend Jacques Charles in
Pilâtre de Rozier’s aerostatic experiments, which crystallized in the ascent of the Marie-
Antoinette balloon on June 23rd, 1784, at Versailles, in the presence of the king Louis
XVI and queen Marie Antoinette of France, Gustav III, King of Sweden, and the French
court. This balloon was built after the experiments of the brothers Jacques-Étienne
Montgolfier (1745-1799) and Joseph Michel Montgolfier (1740-1810). The balloon,
decorated with the French and Swedish coats of arms, floated for about 75 min and
descended without incidents in the forest of Chantilly, at about 52 km from the place of
ascent. The King was so impressed by the results of the manned flights that he awarded
Jacques-Étienne Montgolfier the ribbon of St. Michael, gifted an annuity to his brother
Joseph Michel, elevated their father Pierre to the nobility, and granted the two brothers a
substantial sum to continue their hot air experiments. Proust strongly refused to
participate in a second ascent over the British channel, using a balloon full of hydrogen;
the gas caught fire and Pilâtre and his companion Pierre Romain, fell to their death.
Proust returned to Spain in 1785 to a position offered by the Spanish government,
after being recommended by Lavoisier. In 1778, he was appointed Professor of
Chemistry of the Real Colegio (or Academia Militar para Oficiales y Caballeros
Cadetes de Artillería), installed a few years before in the Alcazar of Segovia. Besides
teaching, he conducted several studies for the government, for example, on the essential
oils of Murcia, detailed studies about the ore of platina and purification of the metal, analysis of the native phosphate of lime of Lograsán in Extremadura, utilization and properties of native Spanish saltpeter and magnesium sulfate deposits.

On June 30th, 1798 Proust married Anne Rose Châtelain d’Aubigné (1778-1817), a French refugee resident of Segovia. They had no children.

On December, 1798 Proust left Segovia after a continuous disagreement with the military authorities of the College. The Spanish government transferred him to Madrid to head a newly organized chemical laboratory that amalgamated the previously existing facilities in Madrid and Segovia, and to offer public chemistry courses. He was allowed to move to Madrid one half of the materials and equipment he had in Segovia. In 1806, he received a leave of absence but did not return to Spain for reasons not altogether clear (one account suggests that it was to settle his patrimony with his brother Joachim), and remained there. The Proust couple settled in Caron, a small village near Angou. Proust spent considerable time at a family farm that he had inherited in the Loire valley. After his wife’s death in 1817, Proust moved to Paris where in 1820 he took over the pharmacy of his brother Joachim, who was in poor health. He then moved to Angers, his birthplace, where he died on July 26, 1826, during an asthma attack. He was buried at the cemetery located in the Château-Gontier Street. As a result of the lack of attention of the administration of cemetery, Proust’s bones were afterwards buried in the common grave of the Grand Cimetière de l’Est.

In 1808, Napoleon's forces invaded Spain; the king Carlos IV (1748-1819) abdicated and during the ensuing political dislocation and resistance the inhabitants of Madrid pillaged Proust’s papers and laboratory during the siege by the French army. This event terminated Proust’s possible return to Spain.

In 1811, Proust was elected member of the Agricultural Society of Turin and in 1816 he was elected to succeed Guyton de Morveau at the Institut de France, by special decree, since he was not resident in Paris, and he was paid the annual grant to members. In 1819, he became foreign associate of the Royal Academy of Sciences of Naples and also a chevalier of the Legion of Honor, and in 1820 he was elected non resident member of the French Académie Royale de Médecine. In the same year, the king Louis XVIII granted him a pension of 1000 gold francs.

According to Esteva, an interesting episode in Proust’s life is the secret and meticulous investigation that the Spanish Inquisition carried on against him between 1780 and 1800. Proust was denounced by Joaquín María de Barroeta, a student at the Seminario de Vergara, of practicing Protestantism, indifference to Catholicism, religious behavior against the church doctrines, not attending mass, and keeping forbidden books. As a result, in 1800 the prosecutor requested Proust’s imprisonment in a secret jail until passing judgment. The fact that Proust was a protégé of the Spanish king and the political events associated with the invasion of Spain by France prevented his arrest and possible torture and death.

Proust wrote, several memoirs on the sugar of grapes and on the methods of preparing it. In 1799, he demonstrated to his class in Madrid that this sugar was identical to that found in honey; honey sugar did not affect litmus paper. It dissolved complete in alcohol and the solution did not react with lead acetate. Nitric acid converted it completely into oxalic acid. Proust suggested the manufacture of grape sugar as a complement to the scarcity of this commodity as a consequence of the continental blockade of England. Proust described the preparation of citric acid, isolated mannitol from manna, and announced the discovery of what he called caseous oxide (oxide caséux, leucine) in cheese and a caseic acid, from the putrefaction of casein.
Proust's main contributions cover a wide variety of subjects: Prussian blue\textsuperscript{24-26}, on tin and its salts\textsuperscript{27-29}, copper and its salts\textsuperscript{30-32}, antimony\textsuperscript{33}, cobalt and nickel\textsuperscript{34,35}, platinum\textsuperscript{12,36}, phosphate rock (apatite)\textsuperscript{13,14}, gun powder\textsuperscript{37}, natural waters\textsuperscript{38}, etc. etc.

**Scientific contribution**

Proust published about 100 papers in Spanish and French journals on inorganic and organic chemistry, food technology, and medical chemistry. Several of these were also published as training manuals and booklets\textsuperscript{1,37-40}. His work on inorganic oxides led him to discover the law of definite proportions.

**Organic chemistry**

**Camphor oil**

In the autumn of 1789, Proust accidentally observed that cold weather had resulted in the partial crystallization of lavender oil.\textsuperscript{11} Believing that the solid was camphor he went on to find if the essential oils extracted from salvia, rosemary, and marjoram (*origanum majorana*) also contained the compound. He found that a simple evaporation of the extracts yielded the same precipitate, although in different proportions: rosemary 6.3 %, marjoram 18 %, salvia 21.1 %, and lavender 25.8 wt %. The crystals dried over filter paper, were pulverulent, bright as snow, and had similar smell, making the identification of the source difficult. He then studied the effect of heat on the original oil, using the fact that their volatility was different. Distillation over a water bath yielded an amount of solid distillate smaller than the one obtained by simple evaporation; the distillate was purified further by means of sublimation. Proust completed his memoir with an economic balance showing that these native essential oils were a cheaper source of camphor that the material imported into Spain.

**Urine**

According to Antoine-François Fourcroy (1750-1809) and Louis Nicolas Vauquelin (1763-1829),\textsuperscript{41} urea constitutes the principle providing to urine with its smell, flavor, and color. Fresh urine blackened silver utensils, cooking them in urine for a long term deposited plates of silver sulfide. After two weeks, urine liberated sulfur together with carbon dioxide. A piece of paper stained with a lead solution and put on the mouth of the bottle blackened immediately, signaling the presence of sulfur. The same phenomenon was observed with solutions of antimony and tin; sulfurous vapors turned the metal salt stain yellow and chestnut, respectively.\textsuperscript{9}

Carbon dioxide was also present in large amounts in urine; Proust believed that urine was the means employed by the body to get rid of all the CO\textsubscript{2} formed during the process of digestion. The release of CO\textsubscript{2} from urine was the reason why urine was always accompanied by froth. Proust examined this froth many times and always found it to be CO\textsubscript{2} mixed with air. For this reason, he concluded that CO\textsubscript{2} must have been the acid factor that saturated the ammonia alkali produced during the putrefaction of urine.

Proust kept for a long time a capped flask filled with urine and opened it every so often to observe possible alterations. He only noticed a slight darkening of color; the urine kept the same odor as fresh urine, all the precipitation formed was the same as that produced by fresh urine in contact with air, meaning that the ammonia alkali of putrefaction was not a necessary factor for this precipitation.\textsuperscript{9}

In summer, urine stored for fifteen days or more and then exposed to air, gave signals of new amounts of ammonia alkali. Addition of a small quantity of sulfuric acid resulted
in abundant effervescence; the CO₂ released carried with itself the sulfur. This meant that atmospheric nitrogen contributed to the formation of ammonia alkali and the affinities that this gas, being the same as that of CO₂ with ammonia, forced the hydrogen of certain putrescible substances to combine. It was probable that the mucilage was the most appropriate source to supply nitrogen to the ammonia alkali. Urine kept in new barrels, deposited prismatic crystals of calcareous carbonate, which effloresced and became powdery when exposed to air.

Proust then asked the question: How come the same carbonate also accompanies urinary stones? To him, the presence of calcium carbonate in these stones and in bones was more than enough to prove that it was present in the precipitate from urine.

Proust indicated that in all at his examinations of the salts present in urine he had never found sodium sulfate, in spite of the opposite affirmations of many chemists. It was true that solutions of barite clouded urine but the precipitate melted very easy with the aid of a blowtorch. Proust felt that still he had to find the presence of barium carbonate. In time of fever, urine on cooling deposited a substance known as latericio (of brick color, rosaceous substance). This sediment was hardly noticeable in a healthy person because it is very soluble in water and its affinity with ammonia kept it dissolved in cold urine. The latericio again dissolved on heating the urine because it is very soluble in warm water and alkalis. This was the reason why the scale formed in urinals was easily eliminated with alkali. But the separation of the rosaceous substance (today, uroerythrin) was accompanied by lithic acid (uric acid) and calcareous phosphate, which were substances composing the sediment that deposits from stored urine. The rosaceous substance saturated alkali but had no tendency to deposit in crystalline form. Nevertheless, it was possible to separate it from them by means of acids in the form of a whitish power, which kept traces of the original color.

Addition of a few drops of nitric acid to fresh urine caused turbidity and precipitation because nitric acid combined with the rosaceous acid substance, yielding an insoluble compound, while the calcareous phosphate remained dissolved. Alkalis also precipitated urine. Precipitation by acids proved that ammonia or any other acid maintained in solution both acids, acting in the same manner as phosphoric acids with calcareous phosphate. 9

Since lithic acid was much less soluble that the rosaceous one, it could be easily separated by washing the sediment with boiling water, followed by filtration. Lithic acid remained on the filter and was easily recognized by its gray color, its granuliform crystalline appearance, and its smell like wet scraped horn. 9

Large amounts of the rosaceous substance could be prepared by passing sizeable amounts of boiling water through the sediment of urine previously collected. The phosphate and calcium carbonate remained in the filter. The phosphate thus separated retained part of the animal substance because added to embers it turned black and released a smell of horn. This same result was observed when treating stones with potash.

Proust also reported that urine contained very small amounts of acetic acid (ácido acetoso). 9

Urinary stones

From 1820 on Proust had the opportunity to make a detailed study of the urine of a girl who had been recently operated from a urinary stone she had carried for about 16 years. The stone was extracted successfully but the patient was left with a suppurating fistula, which had to be continuously drained with a catheter. The oozing liquid was found to leave a white calcareous coating, looking like morning frost, over all the
internal parts carrying the excretion outside the body. A closed inspection of the coating indicated the presence of bright regular grains, arranged like the eggs deposited by insects and indicating that some of crystallization had taken place. According to Proust, this precipitate was simply the material that formed urinary stones, and hence an examination of the urine might reveal the factors that decomposed the stones. His first findings were that the urine of the girl had a specific gravity substantially smaller than that of a healthy woman of the same age (around 1.025 kg/m³). Agitation turned it milky because of the white powder that separated; the filtrate had a yellow color, strong ammonia odor, and turned blue red litmus paper when distilled it yielded a large amount of ammonium carbonate, which effervesced strongly with all acids. It was very probable that the acrid and caustic properties of this salt caused the continuous irritation of the vaginal tube of the patient.

According to Proust, normal female urine treated with nitric acid yielded uric nitrate. This reaction did not occur with the urine of the patient, indicating the total absence of urea and the reason for the lower density of the excretion. In other words, the urinary system of the patient was altered by a chronic malfunction that transformed urea into ammonium carbonate. Other saline components were present in the same amounts as in a normal person.

Proust summarized his findings as follows: The urine of the patient was different from that of a normal female, in having a lower density caused by the absence of urea, the urea being replaced by ammonium carbonate, and by the presence of a large amount of catarrhal mucus. In addition, the action of ammonium urate and calcium phosphate provoked the precipitate mentioned before. Although calcium carbonate was not present in any urine, it was nevertheless found in most stones. It was enough for calcium phosphate to contact ammonium carbonate to have the stone accumulate calcium carbonate.

Uric acid could be separated by addition of HCl but not by addition of nitric acid because the latter transformed it rapidly into CO₂, ammonium oxalate, and ammonium nitrate. An unavoidable result was that the urates, phosphates, oxalates, carbonates, etc., which were always found in a stone, were simply the result of the various saturations caused by the alkalinization of urea.

Proust summarized all his findings on an extensive memoir on the possible causes leading to the formation of urinary stones.

**Citric acid**

A Spanish friend requested from Proust information about the preservation of lemon juice during long sea passages. In his paper on the subject Proust wrote that he was not adding new information about the acid because Carl Wilhelm Scheele (1742-1786) had done it in great detail. Many chemists had tried unsuccessfully to crystallize citric by evaporation. Scheele believed that the failure was due to the presence of impurities that hindered the process. To overcome the problem, he first heated clear lemon juice to its boiling point, followed by addition of chalk (limestone) under continuous stirring. After cooling, lime saturated with acid of lemons (calx citrata) settled on the bottom as heavy powder. The powder was separated by filtration, washed with water several times and then treated with diluted sulfuric acid. The calcium sulfate precipitate was separated by filtration and the clear filtrate evaporated until it crystallized in small crystals.

Proust repeated Scheele’s experiences trying to determine if the impurities present in the juice were the ones that prevented its conservation, and if these impurities could be separated by standard laboratory techniques. Calcium citrate was found to be slightly insoluble in water; the resulting solution was not precipitated by alcohol and not
affected by potassium sulfate, hydrogen fluoride, and phosphoric and boric acids. Precipitation took place with potassium oxalate and oxalic acid. Citric acid was easily separated from the citrate using aqueous sulfuric acid.22

Proust concluded that Scheele’s procedure was applicable to large-scale production of citric acid, as long as all the containers used were made of silver or fine tin. It was absolutely necessary to avoid the use of vessels coated with lead.22

Grape sugar

The history of the development of alternative sources of sugar in France is fascinating and the source of many publications.6,20,44 The first mention of Proust’s work on grape sugar is found on a letter sent to Jean-Claude Delamétherie (1743-1812) in 1802 reporting that he had collected a large amount of sugar extracted from Muscat and expected to find out if this sugar was of the same quality as the one from cane. The answer to the question appeared in a second letter to Delamétherie17 informing that he had found a new sugar (glucose), which was the basis of wine, different from cane sugar (sucrose), crystallized in a different manner, and constituted at least 30 % of Muscat. In an additional letter he added that his assistant had steamed for several days sugar drained of its molasses and was intent in bleaching it as perfectly as possible. Although grape sugar was less sweet than cane sugar, it had a straight and pure taste, without any traces of vegetable flavor or odor. In another letter, Proust described his work on honey and fermentation.18 Eventually, in 1806, Proust published a very long memoir on his findings about grape sugar19 pointing out that this work was a preliminary draft of the art in which grape sugar would play one day an important role. The fermentation properties of grape sugar and its concurrent position with wine were clear advantages; they could open a lucrative market for the excess of grape production. The first part of the memoir described the different known varieties of sugar (cane sugar, beet sugar, honey, manna, different fruits, etc.) as well as their properties. Proust analyzed the components extracted from several Spanish honeys, their consistency, fusibility, solubility in water and alcohol, and tendency to crystallize and precipitate under the action of tin chloride, as well as the action of acids. Compared to sugar cane, raisin sugar was two-and-half times more abundant in the fruits that produced it and 100 % cheaper to collect, extract, and purify. Unfortunately, its crystallization was granular and porous, preventing its solidification like cane sugar; it could only be used as a soft sugar or syrup. Proust used the fact that grape sugar is soluble in alcohol to separate it from the gum and calcium malate that accompanied it and described a method to obtain it raw after deacidification and concentration. He expressed his hopes that the time would come when must of grape would be produced in large quantities and “be a food supplement for the poor and a piece of conversation for the rich”.19

According to McMurtrie,44 the French political situation during the Napoleonic era did much to favor the success of the enterprise. In 1806, Napoleon issued his decrees of Berlin and Milan, establishing the continental blockade of England and excluding from the markets and consumption every material of English production or manufacture, particularly those coming from the British colonies. His intention was to generate an economical and social crisis in England by the lack of grains and by the unemployment due to the failing of supplies of raw materials and the paralysis of exports. England responded in November 11th, 1807, imposing on every vessel traveling to a continental port to stop first in a British port: the North American boats being neutral, promptly renounced to the possibility of seizure, an act that deprived France of its last regular source of sugar. French sugar import of raw sugar dropped from 25000 ts in 1807 to 2000 in 1808; sugar cane became scarce and expensive and pushed forward the search
for alternatives.\textsuperscript{20} The freezing of foreign commerce led to a collapse of the wine trade and the search for alternative uses of the massive crops of grapes that France annually produced. Antoine Augustin Parmentier (1737-1813) had done extensive research about wine and the different products from the vineyard, such as raisins. He promptly realized the importance of the latter as an alternative source of cane sugar, which was coming into France in large quantities as part of the tribute paid by the colonies. He proclaimed the excellence of raisin syrup, having a stronger sweetening power than the solid material, and promoted its large-scale production in France.\textsuperscript{45-47} Parmentier also pioneered the extraction of sugar from beets.\textsuperscript{48,49} Proust and Fouques, a manufacturing chemist, considerably improved Parmentier’s method for extracting and purifying grape sugar. In 1810, Jean-Pierre Count Montalivet (1766-1823), the French Minister of the Interior, informed Napoleon about Parmentier and Proust’s successes in preparing grape syrup and making it suitable to replace cane sugar in many medical and domestic preparations. He also indicated that Fouques had found a mean of bleaching this sugar and giving it not only the brilliancy but also the consistency and color of cane sugar. As a result of this report Napoleon issued a decree (June, 1810) awarding 100000 francs to Proust and 40000 to Fouques “as a gratification and mark of encouragement for their discoveries about grape sugar”. They were supposed to employ these amounts to establish factories for manufacturing grape sugar in the appropriate sections of the southern departments and were ordered to reveal the secret of their procedures. The decree also ordered that from January 1\textsuperscript{st}, 1811 on, grape sugar should replace cane sugar in all public institutions. It is known that Proust refused this subvention although by the same decree Napoleon appointed Proust member of the Legion d’Honneur.\textsuperscript{44} A committee appointed by Montalivet to examine the samples of syrup sugar produced by Proust and Fouques was also ordered to prepare detailed instructions about the methods to be followed for the successful and profitable extraction of syrup and concrete (solid) sugar from grapes.

Interesting enough, the industry proposed by Proust developed considerably, not from the manufacturing fabrication but at the domestic level. The lack of perfection of the fabrication methods and the easy falsification of the must resulted in grape sugar being prepared almost exclusively within the family setting.\textsuperscript{20}

Previous works done on the possibility of manufacturing beet sugar were also recalled. At the beginning of 1811, Montalivet informed Napoleon that it was known that for some years back beet sugar had been manufactured in Berlin and Breslau “...Deyeux, first pharmacist to your Majesty...has re-undertaken this work and has obtained remarkable results...Deyeux is unable as yet to establish the price at which this sugar may be produced. Everything shows, however, that this price will be sufficiently low to prove a large source of profit to extended manufacture...the sugar made by Deyeux...in no way differs from the refined sugar of the colonies”.\textsuperscript{44} This encouraging report led Napoleon in 1811 to issue another decree this time promoting the cultivation of beet. In the same year, Jean-Antoine Chaptal (1756-1832) made an economical evaluation of the cultivar and the manufacture of beet sugar. An interesting item in this report was his statement that promotion of this commodity must be accompanied by a better chemical knowledge of the process. Hence, Chaptal recommended the establishment of “a normal school to train young people in the art and perform chemical research”. On January 1812, Napoleon issued another decree ordering the establishment of three such “special schools for the manufacture of beet-sugar...[the] students shall be selected from among students of medicine, pharmacy, and chemistry”.\textsuperscript{44}
According to Fournier, the end of the blockade caused the disappearance of grape sugar because by being a reducer and fermentable soft solid it could no compete with beet sugar. Grape sugar was usually marketed as syrup, a fact that required its transportation in tanks. Nature also contributed to its failure: the 1809 and 1810 vintages were disastrous leading growers to offer their grapes to those who were willing to pay very high prices.

Leucine

According to Proust, glutine du froment (gluten cheese) was able to ferment spontaneously in a similar manner as sugar substances. In addition to the already known products of these processes, CO₂, acetic acid, and ammonia, cheese produced two new ones, which Proust named acide caséique (caseic acid) and oxide caséeux (caseous oxide, today leucine). Glutine, kept under water at a temperature of about 10 °C, swelled and begun fermenting in less than 12 h producing a gas which Proust found to be composed of CO₂ and (surprisingly) hydrogen. After the gas generation had stopped Proust put the curd under water, in a glass bottle closed by a small plate of glass. No more swelling and gas evolution was observed but the liquid phase was found to contain ammonium acetate, phosphate, and caseate. The same changes were observed when the supernatant fluid was replaced with fresh water. These washings, evaporated in a silver basin and left to stand a few days, solidified into a saline mass slightly transparent and tasting strongly of cheese. During evaporation the surface of the basin was blackened by the H₂S generated.

The three ammonium salts were then dissolved in alcohol; boiling the solution with lead carbonate precipitated the phosphate salt. The remaining lead caseate and acetate were decomposed by hydrogen sulfide and the acetic acid eliminated by distillation.

According to Proust caseic acid had the color and consistency of syrup, an acid bitter taste mixed with that of cheese, and froze into a granular transparent mass like honey. In this state, it reddened litmus paper and did not react with limewater, tin chloride, or lead acetate; it precipitated a solution of silver nitrate, gold nitrate, mercury chloride, and gallic acid, but did not react with the more oxidized salts of iron, cobalt, nickel, manganese, copper, and zinc. Chlorine (acide muriatique oxigéné) did not bleach as it did other animal mucilages, and nitric acid promptly converted it into oxalic acid, a little of benzoic acid and some of the yellow bitter precipitate.

Proust also described the separation and properties of ammonium caseate and caseous oxide. The latter was almost tasteless, soft to the touch, crumbled under the fingers, and when pressed hard it had a peculiar greasy feel. It begun to dissolve in water at 60 °C, was slightly soluble in alcohol, and separated on cooling in crystalline grains. It was insoluble in ether, not attacked by acids and dissolved promptly in potassium hydroxide, without forming soap, and without the KOH losing its causticity. When distilled, it yielded a large amount of yellow oil, which solidified into a smelly fetid greasy paste, smelling like Cadet’s fuming liquor (tetramethylarsine, cacodyl).

Proust ended his paper reporting the analysis of several cheeses and his ideas about the nature of whey and lactose (sucre du lait).

In a paper published in 1827, Henri Braconnot (1780-1855) wrote that no one would contest Proust’s enormous contributions to science, but it had to be accepted that his later works left much to be desired regarding the precision and exactness that should be expected from such a competent chemist. After doing some work on hordein (the largest protein fraction, 40-50 %, of barley storage proteins) and becoming convinced that it was only a compound of starch, animal matter, and ligneous fiber, Braconnot decided to repeat Proust’s experiments on the fermentation of cheese. He took cheese made from
cow milk, well drained but not washed, diluted it with a similar amount of water, and
left it in a covered jar for one month at 20-25 °C. The material was then filtered through
a cloth; the resulting liquid phase was highly colored, reddened litmus paper, did not
show the presence of hydrogen sulfide or ammonium carbonate but retained a
substantial amount of ammonium acetate. Distilled in a retort, it separated into
intensively fetid oil and left a residue containing a white membranous substance, which
on heating coagulated with casein mixed with calcium phosphate. Evaporation of the
coagulum generated acetic vapors and left a syrupy liquid, which diluted in alcohol
separated into two fractions, one formed by *oxide caséeux*, (caseinate oxide) and the
other by ammonium caseinate dissolved in the alcohol. Braconnot made then a very
detailed study of caseinate oxide and was unable to duplicate some of Proust’s results.
For example, according to Proust, caseinate oxide begun to dissolve in water heated
above 60 °C, distillation of the oxide produced very little ammonia, and treatment with
nitric acid gave an abundant crop of oxalic acid and left a little of a bitter substance.
Braconnot found that at 22°C dissolution in water was already complete; distillation
produced a large amount of a fatty material having the consistency of tallow and it also
produced a vapor containing substantial amounts of ammonium carbonate and
ammonium bisulfate. Treatment of the oxide with nitric acid produced no oxalic acid
but the evaporation of the solution generated a bitter yellow oil, from which lime water
disengaged ammonia. To Braconnot, this material had all the properties of an animal
substance, which apparently contained very little oxygen; hence, the name of caseinate
oxide seemed totally inappropriate. Since it appeared to form every time that an animal
substance was left to putrefy Braconnot proposed naming it *aposépédine*, αποσηπεδων
from the Greek απο and σηπεδων (product of putrefaction). *aposépédine* is known
today as leucine.50

Braconnot also repeated Proust’s experiments regarding caseic acid and concluded
that the latter was not a pure substance; the properties attributed by Proust were actually
properties belonging to various foreign substances. According to Braconnot, Proust’s
caseic acid was actually a mixture of free acetic acid; *aposépédine*; animal matter
soluble in water and insoluble in distilled alcohol; a yellow and very acrid oil; an almost
insipid brown resin; potassium chloride and acetate; and traces of ammonium acetate.50

According to Berzelius, cheese, freshly coagulated by an acid, could be solubilized in
water by means of barium carbonate or calcium carbonate.51 Evaporation of the solution
left a residue insoluble in water that Berzelius believed was not the result of the action
of air on the dissolved casein but of the combination of the latter with the earth salt
employed. Braconnot heated white cheese and observed that after some time it
separated into a glutinous elastic mass and serum, from which potash precipitated
calcium phosphate and a small amount of casein. The precipitate was a gelatin-looking
solid, which totally dissolved in cold or boiling water generating liquor that looked like
regenerated milk.50

**Inorganic chemistry**

**Inorganic oxides**

Proust begun his memoir about Prussian blue24 with the question: “If as it is thought,
iron is capable of uniting with oxygen in all possible proportions between 27 and 48%,
which seem to be the two extremes of this combination, why doesn’t it generate with this
acid as many different combinations as it can produce different oxides? Why does this
metal generate with sulfuric acid one salt having constant properties when it is oxidized
to 27%?” There was substantial evidence to prove that iron does not oxidize at states
intermediate between these two limits. The first one corresponded to a green sulfate containing 27% of oxygen, insoluble in alcohol, and not attacked by gallic acid; the second was a red combination, known as vitriol mother liquor, which did not crystallize, was soluble in alcohol, contained 48% oxygen, formed a precipitate with gallic acid, and produced Prussian blue with alkaline prussiates. No other sulfates existed; the green one exposed to air took a color different from that of the two extremes because it was a mixture of both sulfates, which could be separated by means of alcohol. Similarly, it could be proven that there were only two chlorides, two arsenates, two prussiates, etc.

Proust prepared white prussiate by mixing a solution of the green sulfate with a saturated solution of potassium prussiate, showed that it became blue when contacted with air, and described the effect of adding to it sulfuric acid, HCl, and hydrogen sulfide. Prussian blue corresponded to the situation where iron was at its maximum degree of oxidation, that is, the compound contained 48% of oxygen and was converted into white prussiate by the reducing action of hydrogen sulfide or by contact with iron or tin filings. In this memoir, Proust showed that the shade of the product depended on the degree of oxidation of the iron, that is, on the relative amount of the two prussiates of iron. He concluded his paper stating that “these experiments [prove] the principle which I established at the beginning of this memoir; namely, that iron is, like several other metals, subject by that law of nature which presides over all true combinations, to two constant proportions of oxygen. It does not at all differ in this regard from tin, mercury, lead etc. and finally from virtually all of the known combustibles…I will make known the kind of oxide that results from the combination of oxygen with carbon, in a lower proportion to that corresponding to carbon dioxide (carbon monoxide).”\(^24\) In this paper, Proust was expressing for the first time the ideas, which would lead to his law of constants proportions, as shown below.

In his first paper on copper,\(^30\) Proust wrote that in order to determine the amount of oxygen present in mineralized copper oxide it was first necessary to establish the amount of oxygen that copper took when oxidized to its maximum. Using cupric oxide (CuO) originating from different preparations he concluded, “that it must be necessary to accept the conformity found between art operations and those of nature. In practice, oxidation of metals by men is an operation subject to the laws of proportion determined by nature itself, and unchangeable by human design”.

In another paper about copper,\(^31\) Proust reported the results of his experiments on the preparation of copper carbonate, its composition, and comparison with the native material. On their basis he affirmed that the color of hydrated cuprous carbonate was as constant as its properties, independent of the starting material used for preparing it (cupric acetate or cupric nitrate): “...if the base of these two combinations is the black oxide, we must recognize that an invisible hand holds the balance for us in the formation of compounds and fashions properties according to its will. We must conclude that nature operates not otherwise in the depths of the world than at its surface or in the hands of men. These ever-invariable proportions, these constant attributes, which characterize true compounds of art or of nature, in a word, this pondus naturae...(natural law) all this I say, is no more at the power of the chemist than the law of election which presides at all combinations (Note 1) From these considerations is it not right to believe that the native carbonate of copper will never differ from that which art produces in its imitation?

1. George Ernst Stahl (1660-1734) introduced the concept pondus naturæ in 1723.
Is there actually any difference between native carbonate of soda and the natural? No. Why, therefore, should there be any difference between those of copper or of other metals when no other perturbing cause has disarranged the reciprocal forces of the factors of these combinations?"

In two papers published in 1798 and 1804, Proust described his experiences on tin and proved that this metal could only exist in two degrees of oxidation. The first one could be attained by dissolving the metal in cold diluted nitric acid; the second by dissolution in concentrated nitric acid or by the action of heat. He described the preparation and properties of the two tin chlorides (muriates), the reducing action of the lower chloride on indigo (changed its color to green), on cupric salts (sulfate, nitrate, chloride, acetate, and carbonate changed their color to white), etc. In another paper, he proved that antimony and sulfur or oxygen also combined in a dose fixed by nature, which man could not increase or decrease, and described the preparation of the lower and higher oxides by different procedures. The lower oxide was an opaque, crystalline solid melting easily, yielded the ordinary salts, which combined with hydrogen sulfide to yield two products; the highest oxide reacted with difficulty. Both oxides did not react with sulfur.

In paper published in 1804, Proust described the green and white chlorides of copper. The copper oxide containing 35 wt.% of oxygen formed with HCl a green salt having a constant composition. When dissolved in a large amount of water the color changed only from green to blue green, there were no intermediate tones such as brown or white, unless it contained a certain amount of the green chloride. When concentrated by evaporation it crystallized into green filaments, further heating led to loss of crystallization water changing its color to that of cinnamon, in this latter state it could absorb humidity from the air and recover the original color. Additional heating resulted in the release of a thick vapor of oxygenated HCl and a residue of a white powder. Treatment of this powder with a solution of potassium carbonate transformed it after some days the color from white to a golden one, similar to the color of antimony sulfide. The corresponding oxide (copper oxidized to the maximum) contained 25-wt % of oxygen compared with a content of 16.3 wt % at its minimum oxidation state. Once again he stated the law of definite proportions; “We have here like in all combinations of oxygen, new reasons to recognize that law of nature that fixes combustibles and metals in proportions, which we cannot change, not matter how variable are the circumstances of their union”.

In another paper on nickel and cobalt, Proust repeated his claim that these two metals, as many others, existed only in two well-defined states of oxidation; he knew of only two metals (iron and lead), which he had found to exist in more than two oxidized states. It also seemed that the different oxides could dissolve one on the other and form true combinations. Thus, the green cobalt oxide was a combination of the blue oxide and the black oxide.

In a more comprehensive paper about prussiates and Prussian blue, Proust mentioned that metals such as copper, silver, manganese, cobalt, nickel and uranium were able to form simple and triple prussiates, others such as gold and mercury formed only simple prussiates, iron formed only triple prussiates, other metals formed none, and that “with the exception of Prussian blue and mercury prussiate, all the rest are little known, and merit examination”. The law of definite proportions was vigorously opposed by Claude-Louis Berthollet (1748-1822) and gave place to a long and polite dispute with Proust. In his famous book about affinities, Berthollet affirmed that the composition of compounds varied in a continuous manner during a reaction and when changing the experimental conditions.
The cases in which the proportions stopped at fixed values were exemptions and not the general case. Berthollet’s main thesis was that chemical action was due partly to affinity, which he thought of as similar to gravitational attraction, and partly to the masses of the reactants. In his own words: “I have given multiple proofs showing that it is the essence of chemical action to growing in proportion to the amount of substances that exert it and to producing combinations in which the proportions are gradual from the first to the last term of saturation”.\(^5\) To explain the exceptions (constant proportions) he assumed the presence of certain forces that posed an obstacle to the progression of chemical action. Thus in the cases of water and ammonia, two substances originating from the combination of two gases, the chemical action was stopped in the proportion in which the two combined gases were subject to a large condensation. In the case were a solid precipitated from a liquid medium, the cohesion force became preponderant and provoked the separation. For a gas formed from a liquid medium, the elastic tension was the braking source.

The interested reader is referred to some excellent publications discussing in detail the Berthollet-Proust polemic.\(^4,5\) The law of definite proportions has been shown to be a \textit{relative} law. In 1914, Nikolai Semyonovich Kurnakov (1860-1941) reported that during the study of phase equilibrium in metallic systems he had found several instances of intermediate phases with composition varying by several atomic percent of the components. From his results he concluded that stoichiometric compounds should actually be looked upon as special class of phases, which he named \textit{daltonides}. Compounds of variable composition, the non-stoichiometric compounds, formed a more general class of phases, which Kurnakov named \textit{berthollides}. Non-stoichiometry has since been found to be frequently occurring in non-molecular solid compounds. Non-stoichiometric compounds have been found to have a chemical composition varying between certain limits. This phenomenon is characteristic of semi conductors and in substances presenting point defects in their crystalline lattice, such as interstitial atoms and vacancies. A typical example of berthollides is ferrous oxide (wüstide); its ideal stoichiometric formula is FeO but the actual one is close to Fe0.95O. Non-stoichiometric compounds are assumed to be intermediate substances formed in reactions taking place in the solid phase and are a common phenomenon for transition metal oxides. Interesting properties are their being intensively colored and having a chemical reactivity different from the stoichiometric variety.\(^5\)

Beninca\(^5\) uses crystals of nickel oxide (NiO) to illustrate the formation of a non-stoichiometric compound. This oxide crystallizes in a cubic lattice face centered (like sodium chloride), colored pale green and insulating. Heated in an oxygen atmosphere it becomes black. Oxygen atoms locate themselves in the anionic nodes of the lattice and being surrounded by the metallic cations Ni\(^{2+}\) they tend to ionize to anions O\(^{2-}\) by gaining two electrons. The required electrons are furnished by the Ni\(^{2+}\) cations, which pass to the state of Ni\(^{3+}\) ions. This changes the ratio Ni/O to a value slightly less than one, Ni\(_{1-x}\)/O, where the value of \(x\) does not exceed 10\(^{-3}\); the composition is then comprised between NiO and Ni\(_{0.999}\)O. The oxide is then a semi-conductor of type \(p\). The electrical semi conductivity is due to the transfer of electrical charges that occur between two neighboring nickel ions of different charge.

**Platinum**

The word of the existence in Mexico of an infusable metal reached Europe as early as the middle of the sixteenth century. The platinum came from a relatively small area in the Choco district of what is now Colombia. The Spaniards gave the metal the name
platina del Pinto, platina being a somewhat derogatory diminutive of plata meaning silver. Most sources indicated that the first person to make Europe familiar with the name platina was Antonio de Ulloa (1716-1795). In his book about the French scientific expedition to measure the length of a degree of longitude at the equator he wrote: “En el Partido del Choco, habiendo (sic) muchas Minas de Lavadero, como las que se acaban de explicar, se encuentran también algunas, donde por estar disfrazado, y envuelto el Oro con otros Cuerpos Metálicos, Jugos y Piedras, necesita para su beneficio del auxilio del, azogue, y tal vez hallan Minerales donde la Platina (Piedra de tanta resistencia, que no es fácil romperla, ni desmenuzarla con la fuerza del golpe sobre el Yunque de Acero) es causa de que se abandonen; porque ni la calcinación la vence, ni hay arbitrio para extraer el Metal, que encierra, sino a expensas de mucho trabajo y costo.” (In the district of Choco are many mines of lavadero or wash gold, like those we have just described. There are also some mines where mercury must be used, the gold being enveloped in other metallic bodies, stones and bitumen. Several of these mines have been abandoned on account of platina, a substance of such resistance that, when struck on an anvil of steel, it is not easy to be separated; nor is it calcinable; so that the metal enclosed within this obdurate body, could only be extracted with much labor and charge).

E. P. C. Meyer has challenged the claim that de Ulloa was the first to make the mineral familiar in Europe. In a short note published in the journal Science, he reported that the Archivo General de Indias in Seville and the Archivo Histórico y Biblioteca Nacional in Madrid contained references to platinum dating from 1735. Some of these referred to the shipment of rather large quantities (up to 18 pounds) of alloyed material, which was called platina. One document spoke specifically of refined platinum, which had been treated with mercury prior to its shipment to Spain. Meyer also mentioned that the Indians regarded the substance as unripened gold, which they planted “back in the river bed to give it more time to ripen into the golden metal.”

The discovery of the metal led to an intensive research effort by several of the best European chemists; the details of which have been given in another paper and will not be repeated here.

In 1795, Proust published his first paper on the subject in the Anales del Real Laboratorio de Quimica de Segovia, which was reproduced and augmented in a second memoir (Note 2). In the first two sections of this publication, he described the impurities that accompanied raw platinum (stone sand and metallic sand containing gold and mercury; the latter came from the process to recuperate the gold by amalgamation) and the ways to separate them from the metal. The separation was accomplished by simply blowing air at an angle over the material spread on a thin layer. The air pushed the sands, lighter than the platina and gold, to one end, leaving the last two metals essentially free. The gold usually was white because it still retained part of the mercury, making it difficult to identify it. Heating the platina in a crucible volatilized the mercury, the gold recovered its color and platinum looked like burnt iron. Proust indicated that by this process he had obtained 10 % of the gross weight as gold. The separation of the gold could also be achieved by treatment with cold nitric acid, although less efficiently.

He then went on to report the action of heat on the platinum thus separated. When heating with a blowtorch a mixture of powdered metal with carbon released a penetrating smell of sulfur accompanied by smoke.

2. Proust explained that the second journal was more available to the public and that few copies remained of the first journal.
This same result was obtained when heating large grains of platina. Carrying the heating process in a closed crucible produced no smell of sulfur, but the latter appeared as soon as the crucible was opened. Further experiments led him to infer that the sulfurous smell was “hálitos de ácido sulfúrico concentrado” (breaths of concentrated sulfuric trioxide). From these results Proust concluded that the platinum was present as sulfide: “...the platina sulfides do not release their sulfur when heated in closed vessels...the sulfur is not totally released by heating in open vessels because it is contained in the core of each grain, which may be considered a closed vessel”. Thus what was called platinum was actually platinum sulfide. An additional experiment, which seemed to prove the latter hypothesis, was the fact that 800 grains of platina calcined for about one hour lost only one grain; further treated with HCl it gained about 4.5 grains and recovered its white color, “showing that atmospheric oxygen had almost replaced the weight of sulfur driven away”. The acid solution was found to contain platinum, copper, and iron.\(^1\)

According to Moreno García since native platinum ore does not contain sulfur or sulfur containing minerals, the exhalation observed by Proust was probably osmium tetroxide.\(^6\)

The following section described the results of treating platina with aqua regia. Treatment of 400 grains of platinum left 10.5 grains of black residue (2.5 % of the original weight), which Proust assumed to be graphite because it burned slowly with a blowtorch, ignited potassium nitrate, scratched paper bright black, and did not lose its softness when heated under fire. Proust gave a detailed description of his attempts to separate a large amount of the black powder and determined its properties. He also described the crystallization of the supernatant solution, which he believed to be a double salt of potassium chloride and platinum chloride (potassium chloroplatinate, Proust wrote that the potassium of the latter came from the small amount of potassium nitrate present in nitric acid).\(^12\) An interesting fact is that in a letter written in 1804 to Louis Nicolas Vauquelin (1763-1829), describing his findings in Spain\(^6\) Proust confessed that he still did not know for sure the nature of black platinum. In a footnote to this letter Vauquelin wrote that the black residue was not graphite but a new metal (later proven to be iridium).

In the letter to Vauquelin, Proust wrote that he had learned that Hippolyte Victor Collet-Descostils (1773-1815) had searched for a cheaper procedure to extract platinum than the one based on aqua regia and ammonium chloride. His results indicated that a solution of nitric acid and sodium chloride produced platinum chloride, easy to crystallize and separate from iron chloride by the addition of sodium nitrate, which was not decomposed by the platinum salt. Proust believed that the latter procedure could be improved by using sulfides. The black platinum sulfide that precipitated could be easily separated from its sulfur yielding powdery pure platinum, which could be agglutinated and forged easier that the one obtained using ammonium chloride. In a footnote, Vauquelin indicated that Proust procedure would not allow separation of the new metal because it would be contained within a triple salt of platinum, ammonia and chlorine. Proust also mentioned that platinum fulminate might be prepared by decomposing ammonium platinum chloride with KOH and that the fulminate did not easily detonate. Vauquelin commented that he and Fourcroy\(^6\) had prepared platinum fulminate and found it to strongly detonated when gradually heated.

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