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RESUMEN. Bernard Pelletier (1761-1797), un farmacéutico y médico, dedicó su corta vida a la aplicación de la química a problemas prácticos de la industria y la actividad nacional de Francia. Entre ellos se pueden mencionar el comportamiento de las sales deliquescentes, el fósforo y sus derivados, grafito y molibdenita, platino, cobre, cloro, pólvora, jabón, y éteres.

ABSTRACT. Bernard Pelletier (1761-1797) a pharmacist and physician, devoted his short life to the application of chemistry to practical problems of industry and national activity in France. Among them we can mention the behavior of deliquescent salts, phosphorus and its derivatives, graphite and molybdenite, platinum, copper, chlorine, gunpowder, soap, and ethers.

LIFE AND CAREER¹⁻⁴

Bernard Pelletier was born in Bayonne, France, on August 1 (footnote 1), 1761, and died in Paris, on July 21, 1797. The son of Bertrand Pelletier, a master pharmacist, and Marie Sabatier, Bernard begun his education at the local school in Bayonne and then was apprenticed to his father from 1775 to 1778. He then moved to Paris, carrying recommendation letters from his father to his classmate Jean d'Arcet (1725-1801), Professor of Chemistry at the Collège de France, and to Pierre Bayen (1725-1798), apothicaire-major des camps et armés du Roi. The two friends advised Bernard to continue his preparation under Bernard Caubet, a master pharmacist.³ In 1782, after four years of training, d'Arcet's appointed Bernard as his assistant and démonstrateur (lecture demonstrator) at the Collège de France. The chemical researches he carried on in this position led to his first publications on the preparation and properties of arsenic acid,⁵ artificial crystallization of sulfur and cinnabar,⁶ quenching of calcium oxide, decomposition of phosphorus by arsenic acid,⁷ and examination of a zeolite (footnote 2).^{3,4,8}

In 1783 Bernard registered as a student at the Faculté de Médecine de Paris, with the intention of earning a doctoral degree but did not finish his studies there.³ To his luck, in the same year the widow of Hilaire-Marin M. Rouelle's (1718-1779) started searching for someone to manage the pharmacy she had inherited from her husband, located at 45 Rue Jacob. On d'Arcet's recommendation, she hired Pelletier for the job. According to Dorveaux,³ as soon as Bernard was in this position, he tried to be qualified as master pharmacist, although the Collège de Pharmacie required the candidate to be at least 25 years old. Nevertheless, thanks to the protection of Bayen and Antoine Parmentier, an exception to the rule was made and Bernard qualified as a master pharmacist in 1784, after passing the three oral examinations and the practical one. In the same year he married Marguerite Sédillot, the sister of his friend Jean Sédillot 1757-1840) a physician who later on would become master surgeon in Paris. In the same year Pelletier bought the Rouelle pharmacy, changed its name to Pharmacie Pelletier, and held it until 1836. One of his two sons, Pierre Joseph (1788-1842), also grew to become a pharmacist, professor, and famous scientist for his researches on alkaloids, natural products, and vegetable dyes, in collaboration with Joseph Bienaimé Caventou (1795-1877). Warolin has published a short paper describing how the address (and owners) of Pharmacie Pelletier in Rue Jacob changed from the original #15 to the present one #48, along the different stages of French history.⁹ Anyhow, the intense research activity of Bernard Pelletier forced him to transfer the management of the business to his brother Charles.

[1] Dorveaux reproduces the baptism certificate of Bernard Pelletier where it says that Pelletier was born on August 1, 1761, and not on July 31, as reported in most of his biographic information.

[2] Many of Pelletier's memoirs and reports were published in abridged form in the *Journal de Physique* of the Abbé Rozier. The reader is referred to the book by Pelletier and Sédillot et al. for a full version (1798).

One of the most important research projects of Bernard was carried on in 1784, when he succeeded in preparing and describing the crystals of several very soluble or deliquescent salts.¹⁰ Among the many salts studied were potassium carbonate, ammonium acetate, ammonium nitrate, calcium nitrate, calcium chloride, magnesium acetate, magnesium nitrate, magnesium chloride, aluminum nitrate, zinc acetate, zinc nitrate, cuprous chloride, and cuprous nitrate. The following year he read to the Académie an extensive memoir about graphite and molybdenite (MoS_2)¹¹ (more than 80 pages), another where he repeated Carl Wilhelm Scheele's (1742-1786) experiences showing that dephlogisticated marine acid (chlorine) is released during the reaction of marine acid (HCl) and manganese calx (dioxide),¹² a third memoir about the formation of ethers,¹³ and a fourth about the reactions of phosphoric acid.¹⁴

This intensive rate of publication was deliberate because of a coming election for membership in the classe de chimie (chemistry section) of the Académie des Sciences, although once again, Pelletier was below the age required for admittance (25 years). He ran against Antoine-François Fourcroy (1750-1809), Henri Louis Duhamel du Monceau (1700-1781), and Philippe Gengembre, and lost (Fourcroy was elected). In spite of this defeat, the following year he tried again, this time in the classe d'histoire naturelle (natural history section), and once again failed (Duhamel won this election).

Pelletier's following publications were about ethyl acetate and salts,¹⁵ phosphorus and its derivatives,¹⁶⁻¹⁸ ethyl ether¹⁹ extraction of copper from bells for the manufacture of coins,²⁰ etc.

As told by Dorveaux,³ in 1783 Pelletier matriculated as a student in the Paris Faculty of Medicine but did not graduate there. In 1790, however, he made two journeys to Rheims where he passed the examination for his doctorate in medicine. On May 1790 he read to the faculty his thesis for obtaining the baccalauréat, entitled *An aer ex camino, gallicé la cheminée; an aer ex hypotecausto, gallicé le poêle, sit salubris?* (Which air is healthier, the one heated by a chimney or the one heated by a stove?). The answer was: the air heated by a chimney. In July of the same year he returned to Rheims to read his *thèse de license* entitled *Litteratis ne salubrious café usus?* (Is coffee drinking valuable for literature?). The following day he defended successfully his general thesis and was proclaimed doctor.³

In 1792 Pelletier presented his name as candidate to replace Antoine-Laurent Lavoisier's (1743-1794) as pensionnaire chimiste in the class of chemistry of the Académie des Sciences, based on the rule that stated that at least one of the candidates must be someone who is not a member of the Académie.³ Pelletier was now 30 years old, had published a large number of valuable papers, and was well known in the scientific community. Once again he was defeated, the Académie selected Claude-Louis Berthollet (1748-1822) for the position. This result left Berthollet's position as associé chimiste (associate chemist) open. The candidates were Pelletier, Armand Séguin (1767-1835), Louis Nicolas Vauquelin (1763-1829), and Jean-Henri Hassenfrantz (1755-1827). This time Pelletier succeeded and his nomination announced on March 19, 1792. An interesting fact is that this event took place one year the year before the suppression of the Académie by the Convention.³ When the Académie was reopened in 1795 under the name Institut National, Pelletier was elected as member of chemistry section of the First Class.^{4,9}

To support his candidacy Pelletier presented to the Académie his research on the reaction of tin with sulfur,²¹ the combination of phosphorus with metals,²² the properties of tin chloride,²³ the preparation of phosphoric and phosphorous acids,²⁴ the analysis of potassium carbonate,²⁵ and the analysis and preparation of blue cinder (a blue copper mineral).²⁶

In 1794 the National Convention, under the leadership of Lazare Carnot (1753-1823) and Gaspar Monge (1746-1818), established the École Centrale des Travaux Publics, which a year later would change its name to École Polytechnique. The object of the school was to provide its students with a solid scientific education based on mathematics, physics, and chemistry and to prepare them for entry into the special Civil Service schools such as the École d'Application de l'Artillerie et du Génie, the École des Mines and the École des Ponts et Chaussées. In 1804 Napoleon transformed it into a military school under the motto "Pour la Patrie, les Sciences et la Gloire" (for the fatherland, sciences and glory). The most distinguished scientists were hired to become the first teachers. Pelletier was appointed assistant professor of chemistry and collaborated with Louis-Bernard Guyton de Morveau (1737-1816) with the course on mineral chemistry.

Pelletier was appointed member of many important public committees; Inspector of the military hospitals in the Netherlands, Health Council of the Armies, Commissary of Gunpowder and Saltpetre, Bureau de Consultation des Arts et Métiers and of the Commission Temporaire des Arts. Within his tasks was the preparation of reports related to national needs, particularly in those conflictive political and military days. Among them we can mention a description and analysis of the different processes for manufacturing sodium carbonate; particularly the one of Nicolas Leblanc (1742-1806) and Jérôme Dizet (1764-1852),²⁷ on Marc Étienne Janety's (1739-1820) process for manufacturing malleable platinum,^{28,29} on Séguin's method for tanning leather,³⁰ on Grenet's method for producing animal glue,³¹ the production of soap and the necessary reagents,³² the recycling of waste paper,³³ and the recycling of copper from church bells.³⁴ Pelletier also served in the commission of the Institut (the old Académie of Sciences) that investigated methods of refining and analyzing saltpeter for gunpowder manufacture, but he had already contracted pulmonary tuberculosis and died on July 21, 1797, before his work was completed.⁴ According to Sédillot¹ his pulmonary problems were a result of the many different metal and carbon vapors he had inhaled during his research work.

SCIENTIFIC CONTRIBUTION

Pelletier published over 50 papers and reports on the different subjects he was involved scientifically and politically. Most of them were recollected by his brother Charles and his brother-in-law Jean Sédillot and published as a book in 1798.³⁵

Soap manufacture

On July 11, 1795, the Comité de Salut Public (Committee of Public Safety) of the National Convention charged d'Arcet, Claude-Hugo Lelièvre (1752-1835), and Pelletier to carry on “des expériences sur l'union de différentes espèces d'huiles et de graisses avec la soude, de faire connaître au comité les savons qui résultent de ces combinaisons, leur nature, leur qualité, etc.” (Experiments on the combination of different kinds of oils and fats with soda in order make known to the committee the soaps that resulted from the combinations, their nature, their quality, etc.). The result of their work was the almost 100 page long “Rapport sur la Fabrication des Savons” published in 1797.³² The first part of the report described the sources, different kinds, methods of preparation, and characteristics of the raw materials required (sodium hydroxide, potassium hydroxide, calcium hydroxide, and oils and fats), as well as the equipment necessary for the different operations. This was followed by procedures for the preparation of soda and causticized lye, the apparatus for preparing the lye and for soap boiling operation; the characteristics of the resulting soaps, and the instruments used for measuring the strength of the lye. Detailed instructions were given for the fabrication of soaps based on olive oil, almond oil tallow, axunge (the rich internal fat of the kidneys, etc.), rancid butter, horse grease, navette oil, poppy seed oil, hemp oil, beechnut oil, linseed oil, fish oils, Their results indicated that the different varieties of oils and fats were not equally appropriate for manufacturing solid soaps, and hence they could be classified as follows, in decreasing order of fitness for this purpose: (1) olive and sweet almond oils; (2) tallow, lard, rancid butter, and horse oil, (3) rapeseed and navette oils, (4) beechnut and poppy seed oils, (5) fish and whale oils, (6) hempseed oil, and (7) beech nut and linseed oils.

D'Arcet, Lelièvre, and Pelletier also described the methods for making hard soaps from potash soaps by the addition of salt solution to the soft soap and boiling the mixture for several hours. They also considered the methods for making fraudulent soaps, particularly by the addition of large amounts of water, salt, alum, starch, chalk, and lard. According to them, the only way of identifying the adulterants was by analysis.

The final part of the report was a set of instructions for those who wanted to make soap by themselves.

Chevreul made a thorough study of the saponification process using a variety of bases such as soda, baryta, lime, and metal oxides and also showed that acetic acid and carbon dioxide were not products of saponification, but were in fact impurities in the reagents.³⁶ He also proved that soaps could be formed in the absence of air and concluded that oxygen was unnecessary thus giving a mortal blow to the theories of Pelletier and others. For example, Fourcroy claimed³⁷ that the formation of soaps and plasters was due to the oxidation of the oil under the influence of alkalis or metallic oxides and, consequently, had put all the oils and fats in a generic group designated as *adipowax* (*adipocire*) to be considered as species of fixed oxidized oil.

Copper

In order to try to solve the monetary deficit, the Assemblée Nationale Constituante decreed in 1789 that all the ecclesiastical property should be put at the disposition of the Nation; as a consequence, many churches fell in disuse and a large number of bells came into the market and with them the interest in the large quantity of copper available in the form of bell metal, an alloy containing 20 to 25 % of tin. Several possibilities were considered for their use: to sell them as such, to separate the components, or to alloy them with a certain amount of copper in order to make them ductile enough so that they could be used to manufacture cannons, coins, or statues. According to Pelletier some people believed that it was impossible to separate pure copper from the alloy. In 1791 he communicated the Comité de Monnaies (Currency committee) the results of his experiences, proving that the separation was feasible. His method was based on heating molten bell metal with manganese dioxide; the latter being added in small portions during several hours. His experimental results indicated that 100 kg of bell metal yielded 75 kg of copper.²⁰

Fourcroy³⁸ and d'Arcet in collaboration with Pelletier,³⁴ made the most important contributions to the subject. D'Arcet and Pelletier's method was also based on the oxidation of the bell alloy with manganese oxide, which attacked the tin before the copper and gave a good yield. Fourcroy's approach was in two different directions, based on the variable affinity that oxygen has for metals. In one of them, the bell metal was heated in a crucible in the presence of air until the increase in weight showed that sufficient oxygen had been absorbed to oxidize all the tin, followed by heating the molten metal in a closed crucible, avoiding the possibility of further absorption of oxygen. During this second heating stage the copper oxide was reduced by the unreacted tin and at the end of the reaction all the tin was oxidized and could be separated from the molten copper. Fourcroy's second approach was based on the oxidation of the tin by heating the alloy with certain metallic oxides; he achieved good separation with black oxide of manganese but litharge and oxide of arsenic were found to be unsatisfactory.

As a result, in 1793, when large quantities of copper were urgently needed for manufacturing cannon, the Committee of Public Safety decreed the requisition and usage of all church bells for the making of bullets. Instructions describing both Pelletier's and Fourcroy's methods were published in detail and both were

recommended. Fourcroy's procedure proved to be cheaper, although equally helped provide copper to the revolutionary government during the many wars it held during its existence.³⁴

Pelletier's unconditional support of the strong relation between science and Revolution are clearly stated in the introduction to his Instruction: "All the sciences, all the technologies, all the knowledge possessed by the French at the highest level, must converge at this moment to the strengthening of the Republic, one and indivisible, to the destruction of her enemies, which through an impious war oppose the success of our glorious revolution...Physics and chemistry must contribute their researches to the defense of such a beautiful cause...It is believed that there is a shortage of copper or the available stocks are insufficient to satisfy the requirements for weapons use. Before the necessary research will teach us how to successfully exploit the mines contained in our territory, the chemical art must teach us how to benefit from what is already available. A bell, with which superstition has over loaded churches, offers us a fruitful resource, a kind of mineral abundant enough to satisfy our needs. We have to learn how to separate copper from them; this is the purpose of this instruction".³⁴

Phosphorus

According to Pelletier,¹⁷ Andreas Sigmund Marggraff (1709-1782) had tried to combine phosphorus with metals, but had failed because of the experimental procedure he had followed. He had distilled a mixture of phosphorus with several metals without taking into account that the reaction required that the metals be in a liquid state. Phosphorus had completely distilled away before the metal had achieved the required temperature. Thus Marggraff had reached the wrong conclusion that phosphorus had no action on copper, zinc and arsenic. Pelletier believed that the strong similarity between sulfur, arsenic, and phosphorus suggested that the latter should combine with metals, and the only obstacle was the operating procedure. In principle the metal had to be first melted before addition of phosphorus, but this was fraught with danger. To avoid this problem, he decided to use phosphoric glass (footnote 3) as the source of phosphorus, instead of using the pure element. Thus he mixed the metal with phosphoric glass and carbon and heated it in a crucible to a temperature high enough to cause fusion. His first experiments were with gold. During heating most of the phosphorus evaporated but a small part combined with the metal yielding a highly fragile white solid, which lost its phosphorus on continuous heating. Similar results were obtained with silver, platinum, copper, iron, lead, and tin. The phosphides of silver, platinum, copper, and iron were less ductile than the pure metal; those of lead and tin retained the original ductility. In addition, heating the phosphides resulted in the release of phosphorus either as a vapor or burning on the surface of the phosphide. Copper phosphide in contact with air lost its brilliancy and acquired a black color. Pelletier's explanation of the results was based on the affinity of oxygen with carbon being larger than that with vitreous phosphoric acid (phosphorus pentoxide). Carbon paired with oxygen of the acid forming a new combination, carbon dioxide, which separated as a gas. The remaining base of phosphoric acid, that is, phosphorus, combined with the metal present, unless enough heat was applied to destroy the new combination.

In a following memoir Pelletier extended his study to the reaction of phosphorus with sulfur.¹⁸ A given amount of phosphorus was heated under water until it melted and then different amounts of sulfur added. The product was liquid at room temperature but solidified when the temperature was low enough. The reaction could also be carried on by distillation, without the presence of water; it was very fast and many times it resulted in an explosion which shattered the flask. Pelletier concluded that phosphorus combined with different amounts of sulfur and the product was decomposed by water. During this decomposition the water became acid and a fetid gas was released, which was luminous in the dark.

An interesting point is that the explanation given by Pelletier shows how he was switching from the phlogiston theory to the new theories of Lavoisier: "According to the new doctrine water must have decomposed. One of its principles must have joined with the combination of sulfur and phosphorus and produced acids analogous to these two bases or acid radicals. The inflammable air (oxygen), another principle of water, becoming free, has to liberate, entrain with it, or hold in solution, part of the sulfur and of the phosphorus that have not decomposed, giving thus birth to the particular fetid gas, that reminds the smell of gas hépatique (H₂S); the phenomena of this decomposition can also be explained by Stahl's theory (phlogiston)".¹⁸

Three years later Pelletier reported additional results about the combination of phosphorus with metals.²² He had already noted that metals easily oxidized, enjoying like carbon of the property of removing the oxygen from phosphoric acid. This observation had provided Pelletier with a new procedure for preparing phosphides: treating the metals with phosphoric glass in a fused state. This time he wanted to prepare phosphides by the direct reaction between the fused metal and phosphorus. He took care of advising the reader to take the proper precautions because of the risks involved in such procedure.

[3] Phosphoric glass was prepared by Jean-Antoine Chaptal (1756-1832) by boiling bone with sulfuric acid, followed by evaporation to dryness, washing with water, another evaporation to dryness, addition of water and filtration of the calcium sulfate. The latter was treated in a crucible until luminescence subsided. The remaining material was a milk white glass.

This time he melted the metal in the crucible and then added to it phosphorus in very small pieces. Application of this method to gold, platinum, copper, iron, lead, and tin, yielded a larger amount of gold phosphide than when using phosphoric glass and carbon (as explained above). The results with silver were surprising, the phosphorus would melt and completely mix with the melted silver, but on cooling, when the mixture would stop being fluid, it would liberate a large amount of phosphorus, which would burn in contact with air. Pelletier understood that in the liquid state silver remained combined with phosphorus in a much larger proportion than when in the solid state.²²

Pelletier also studied the phosphorization of mercury, zinc, bismuth, antimony, cobalt, nickel, speiss (a molten phase consisting primarily of iron arsenide), molybdenum, tungsten, manganese, and arsenic. He could not make mercury to react with phosphorus in direct contact but he was able to prepare the corresponding phosphide by reacting mercury red oxide (HgO) with phosphorus water. The dry phosphide, in contact with dry air was seen to release white vapors smelling like phosphorus.

Pelletier ended his memoir stating that his experiences proved his original thesis that phosphorus, the same as arsenic and sulfur, combined with metals, and behaved exactly like arsenic. It also appeared that phosphorus was able to combine with metal oxides and probably these combinations were present in the mineral kingdom.²²

A following publication related to the preparation of phosphorus and phosphoric acids (phosphorus trioxide and pentoxide), and sodium phosphate.²⁴ Pelletier indicated that the best methods for preparing the two acids were those of Balthazar-Georges Sage³⁹ (1740-1824), and Lavoisier,⁴⁰ respectively. Sage's method was based in putting cylinders of phosphorus on the walls of a capped funnel and heating slowly. Without the cap the phosphorus would catch fire and yield pentoxide. Lavoisier's procedure was simply burning the phosphorus in contact with air.

To avoid the explosions that frequently occurred with Sage's method, Pelletier put the cylinders of phosphorus inside small glass cylinders opened in the bottom as a funnel, to let the acid formed flow out. These small tubes were located on the inside walls of a large funnel. Pelletier (a pharmacist) believed that medicine could benefit from the derivatives of the oxides. For example, sodium phosphate was prepared by reacting sodium hydroxide with phosphoric acid. It was found that this salt had many of the properties of borax; it was very soluble in water and had a pleasant flavor. The saturated solution turned green violet syrup. It crystallized in a variety of forms, forming different hydrates; it was highly transparent, etc. etc. Sodium phosphate was used as a purgative and could be employed in welding, replacing, borax, an expensive imported material.

In 1816 Pierre-Louis Dulong (1785-1838) proved that there are at least four distinct acids formed by the combination of phosphorus with oxygen. The acid with the minimum of oxygen (hypophosphorus acid) was prepared by reacting alkaline phosphides with water, particularly barium phosphide. The composition of the acid could not be ascertained by direct analysis because none of its combinations could be obtained in the dry state. Dulong determined it (72.75 % phosphorus and 27.25 % oxygen) oxidizing the compound to phosphoric acid with chlorine.⁴¹

In 1790 Pelletier and Louis Donadei made a thorough study of a sample of rock phosphate (apatite) originating from Extremadura, Spain.⁴² They first described the mineral pointing out that it contained quartz and small grains of metallic pyrites, which they believed to be iron phosphide. The crushed rock showed traces of luminescence in the dark, and also when it was rubbed with an iron blade. The same phenomenon was observed when a finely ground powder was thrown on burning coal. Treatment with boiling water dissolved a small amount of salt that proved to be calcium chloride; the remaining solid retained its luminescence property. The rock treated with concentrated sulfuric acid released a white vapor smelling like marine acid (HCl), which etched glass. Analysis of the vapor proved that it contained *gaz fluorique* (HF) and HCl, and analysis of the remaining solid showed that it contained phosphoric acid. Distillation of the mixture of apatite + sulfuric acid resulted in the deposition of a red solid on the neck of the flask, very acid and avid of humidity, and which Pelletier believed was phosphorus acid. The rock dissolved almost completely in boiling nitric acid; the remaining solid residue was not phosphorescent. The rock easily dissolved in HCl; when using concentrated acid, the final product was gelatinous. As a result of all the tests, Pelletier and Donadei concluded that the Extremadura apatite contained 59 % wt. calcareous earth, 39 % phosphoric acid, 2.5 % hydrofluoric, 2 % quartz 2 %, and small amounts of oxygen, iron, and nitrate. They speculated that the simultaneous presence of HF and phosphoric acid combined with calcium suggested the possibility that HF was a modification of phosphoric acid (!). In addition, they expressed their belief that phosphoric acid equally belonged to the animal and the mineral kingdom.⁴²

In a following note Pelletier reported an accident that had occurred while studying the phosphate rock brought from Spain. While doing experiments on phosphine, Pelletier introduced the gas in a cylindrical bell held inside a water basin and noticed that it did not dissolve. Nothing particular happened when he added an equivalent volume of air, of oxygen, or of nitrogen dioxide but when he started adding nitrogen dioxide to a mixture of phosphine and oxygen an instantaneous explosion took place that reduced to fine pieces the part of the bell located under the water. Pieces of the glass hit Pelletier's eyes, fortunately without permanent damage. In his paper about Pelletier, Dorveaux describes a second accident that took place in another opportunity.³ At one time Pelletier was tidying the laboratory with his students; one of them showed him a piece of folded paper he had found, containing what looked like a solid. Ignorant of its composition (it was phosphorus), Pelletier put the folded paper inside his pocket. Due to the proximity to his body and the friction, the phosphorus attained the inflammation temperature and set Pelletier's clothes on fire, ran along his thighs and caused him great damage. Unable to control the situation, the students called for help. The first to

arrive was Bayen who treated Pelletier as best as possible. It took Pelletier six months of intense suffering to recover from his wounds.

Platinum

The first platinum to be subject to scientific investigation by European scientists was brought in 1741 from Cartagena (Colombia) to England by Charles Wood (1702-1774). Wood presented the specimens to William Brownrigg (1711-1800) who passed the samples on to William Watson (1715-1787) and asked him to communicate his findings to the Royal Society, which he did in 1749.⁴³ Wood did carry out some experiments and found that platina could not be melted at any temperature then obtainable even by adding to it borax or other saline fluxes. In 1752 Heinrich Theodore Scheffer (1710-1759) made the important discovery that addition of a small amount of arsenic to a much larger quantity of platinum brought its complete fusion at relatively low temperatures.⁴⁴ In 1757 Marggraff repeated some of the experiments done by others and again observed that at a very high temperature platinum grains only sintered together and were easily broken up by hammer blows.⁴⁵ Franz Karl Achard (1753-1821) heated a mixture of platinum with arsenic and potash and obtained a metallic button, which when heated in a muffle to red heat released the arsenic in the form of white fumes. The solid remaining after the fumes had ceased was fully malleable and ductile as gold. Achard understood that this procedure allowed manufacturing "all kinds of small vessels and especially small fusion crucibles which can be useful in certain operations".⁴⁶ The arsenic procedure was used by Alexis Marie Rochon (1741-1817) to produce the platinum crucibles needed in the construction of his reflecting telescopes.⁴⁷

As mentioned above, Pelletier prepared the phosphides of many metals, one of them platinum. The results led him in 1788 to propose a method, similar to the one based on arsenic, to make malleable platinum.¹⁷ Pelletier's method consisted in strongly heating a mixture of native platinum, phosphoric glass [3], and carbon, in a crucible for one hour at the temperature of fusion of gold. After cooling the mixture Pelletier found a small white button on top of black glass. In the bottom part of it were cubic crystals. He repeated the experience several times and always found a mixture formed of black glass, carbon, and platinum. The latter was always allied with phosphorus; this alloy was very hard, nonmagnetic, and had a sour taste. Heated to its fusion temperature it released the phosphorus, which burned on the surface leaving a black glass that surrounded the metal. According to Pelletier the black color was due to the iron contained in the platinum. Repeating this experience several times the glass produced changed its color from black to clear white; indicating that phosphorus was able to separate completely the iron from the platinum. The final platinum was cooled, hammered, and found to be highly malleable. Heated while being hammered it shattered and heated further over burning coal it released white vapors showing that it still contained a little of phosphorus. These results led Pelletier to develop an improved method to produce very malleable platinum: Once most the phosphorus had been eliminated as described above, the metal was dropped into melted sulfur several times, and thus deprived of all the iron it contained.

Pelletier gave the platinum he had manufactured to Janety, a Paris goldsmith, who used it to manufacture balance pans, which Pelletier gave to the Académie des Sciences.

Pelletier mentioned that many craftsmen, including Janety, used arsenic to melt platinum. He believed that this method was less expensive than his, but very dangerous to the workers and deterred people who wanted to use platinum for home purposes. His procedure could be used without fear and to prepare large amounts of platinum. He ended his report expressing his belief that a mixture of charcoal and many salts based on phosphoric acid (phosphorus pentoxide) could be used to phosphorize platinum. An interesting observation was that adding a mixture of platinum phosphide and potassium chloride to a red-hot crucible resulted in a strong explosion leaving pure platinum in the crucible. The same result was obtained when platinum phosphide was added to a melt of potassium nitrate.

Around 1784 Janety became interested in the means of working platinum. To make malleable he utilized the known procedures of Marggraff, Achard, and Scheffer, based on alloying the metal with arsenic in the presence of potassium hydroxide. He would melt the materials together until all the iron had been removed. Further heating at a higher temperature caused the arsenic to evaporate leaving malleable platinum. Being a well-known craftsman in working gold and silver, he now added platinum to his starting materials. The Académie des Sciences bought from him a bar 14 feet long, two bars 19 feet long each weighing 22 marcs (5.4 kg), another bar 19 feet long, a ball weighing 18 marcs (4.4 kg), and a concave mirror weighing 12 marcs (2.9 kg). For the private market he made small articles such as snuffboxes, watch chains, tableware, coffee pots, etc. In 1792 the National Assembly created the Bureau de Consultation des Arts et Métiers for encouraging the work of artisans and supporting those in need of help. In 1792 Janety applied for an award for his method of making malleable platinum; the Bureau de Consultation appointed Pelletier and Berthollet as referees to evaluate his claim. The two wrote a very favorable report, pointing out that by having Janety introduced in the market such a precious and useful metal, gave him all the rights to receive a national reward.²⁹

Chlorine

Pelletier's experiments with hydrogen chloride and chlorine show that at that time (1784) he supported the phlogiston theory.

According to Scheele, marine acid (HCl) could be dephlogisticated by distillation over manganese (this is the name given then to the dioxide), a calx so avid of phlogiston that it could remove it from the acid. Pelletier repeated Scheele's experiments and was amazed to see the aspect of marine acid after dephlogistication, and of the phenomenon

that accompanied the process, particularly effervescence and release of heat. Dropping a burning candle abruptly on the gas, it was blown out but introducing it in such a way that the flame licked the surface of the dephlogisticated air, its aureole became green. The gas released was totally absorbed by water and the remaining air allowed a candle to burn in the normal manner. For all these reasons Pelletier decided to use try to separate the gas released by other acids. Thus he heated manganese dioxide with sulfuric acid, nitric acid, and aqua regia, as well as studied the absorption of dephlogisticated air by marine acid, and the reaction of the latter with mercury. His results with sulfuric acid produced dephlogisticated air and a solid residue that he identified as manganese sulfate. He believed that the air was not due to the decomposition of sulfuric acid but to manganese calx that held it as one of its constituent parts; an observation confirmed by Joseph Priestley's (1733-1804) experiments by which he obtained dephlogisticated air by simple distillation of the calx. Priestley also distilled a mixture of calx and sulfuric acid and obtained fixed air (CO₂) instead of dephlogisticated air, because he carried the reaction inside the cannon of a rifle. Nitric acid attacked the calx only when loaded with gas nitreux (nitrous oxides), produced by adding sugar to the acid.

Scheele had named the gas released dephlogisticated marine acid and reported that it dissolved gold and mercury and smelled like aqua regia.

Pelletier found that mixing dephlogisticated marine acid with gas nitreux made both immediately visible and absorbed by water. From these results he inferred that the phenomena observed during the preparation of aqua regia were exactly the same as those seen during the dephlogistication of marine acid by calx. He also found that marine acid did not attack mercury because the acid was not saturated with dephlogisticated air. In other words, it was possible to carry the reaction by mixing the acid with mercury combined with dephlogisticated air (mercury oxide). A red precipitate appeared, which was soluble in marine acid.

In the final part of his memoir, Pelletier wrote that his experiments proved that part of the inflammable air (oxygen) combined with dephlogisticated air (chlorine) to form a new entity that was absorbed by water. He also described his experiments on the reaction of concentrated marine acid with vinegar, in the presence of manganese calx, and his belief that he had produced marine ether.

Sodium carbonate

In 1794 the Comité de Salut Public wrote to all French manufacturers of sodium carbonate that France being at war, the manufacture of sodium carbonate had become a matter of national interest. Consequently, "it invited all citizens who had made some trials, who have collected some observations of the subject, to communicate them to the committee which it has established to receive them, and which is charged to analyze them and to report its conclusions". A following decree was more draconian: "All citizens who have established factories or obtained patents for inventions to make soda from salt, are hereby ordered, even though they are planning to enlarge these establishments as much as possible, to make known to the commission, within two decades (20 d), the location of these plants, the quantities of soda they put on the market, how much they can furnish, and the date at which they can start their deliveries."

After all the required information was collected, a special committee constituted by Claude Hugues Lelièvre (1752-1835), Pelletier, d'Arcet, and Alexander Giroud was appointed to analyze the information, examine the processes, run pilot experiments and to inspect the manufacturing facilities. Their almost 100 page long report,²⁸ published in June 1794, reported the visits to the facilities of Leblanc, Dizé, and Shée (located at Franciade) and of Alban (located at Javelle), the results of pilot experiments with their methods, as well as an analysis of the proposals submitted by Malherbe and Athénas, Chaptal and Bérard, Guyton and Carny, Ribacourt, by Souton, Duboscq and Huon, and by Valentino. The committee was most impressed by the Leblanc process and believed it probably was the one that should be adopted: to "*Nous avons visité cet atelier naissant...et nous avons vérifié le procédé, sur lequel nous croyons pouvoir déjà prononcer avec la plus grande certitude de succès. Ce nouvel établissement a été élevé en entier sur ses propres fondements, et avec la prudence et la circonspection qu'on pouvoit attendre de l'intelligence et du bon esprit des trois associés...Le procédé du citoyen Leblanc, par l'intermède de la craie, nous paraît celui qui peut être le plus généralement adopté; parce que cette matière première est plus universellement répandue; elle a de plus cet avantage, qu'elle n'empêche pas la soude d'être mise dans le commerce, dans l'état brut; qu'elle ressemble plus particulièrement à celle que le commerce nous procure de l'étranger...qu'elle peut s'appliquer immédiatement et sans lessivage préliminaire, à la buanderie, à la verrerie commune, et à la confection du savon*" (We have inspected their establishment...and we have verified their process and we believe it is certain to be successful. This new facility has been established on correct principles from start to finish and has been set up with the prudence and circumspection that was to be expected from the intelligence and good sense of the three partners... The process of citizen Leblanc, which uses chalk as the intermediate, appears to us to be the one that could be most generally adopted, because this raw material is most widely distributed. The process has the added advantage of supplying a product that can be marketed in the crude state; the product is quite like that which comes from abroad... it may be used directly and without preliminary purification for bleaching, for ordinary glass, and for making soap).

In spite of France being at war, the detailed report (and Leblanc's patent) was made public. It contained a thorough description of all the processes, their operating procedures, and equipment (particularly those of the Leblanc factory). After the war the British got hold of the report, started their own manufacturing facilities, and eventually became the largest producers of sodium carbonate.

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