

RESEÑA BIOGRAFICA

Théophile-Jules Pelouze. Glass, wine and explosives

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RESUMEN. Théophile-Jules Pelouze (1807-1867) fue un destacado químico analítico y experimental que trabajó en una variedad de áreas industriales tales como la salicina, azúcar de betarraga, tanino, ácido pirogálico, nitrocelulosa, fermentación butírica, fabricación del vidrio y curare. Nos dejó como herencia métodos de análisis y producción para estos productos, pero muy poco en el aspecto teórico. Sus trabajos sobre nitrocelulosa constituyeron un elemento importante en el desarrollo de la producción de nitroglicerina por Alfredo Nobel.

ABSTRACT. Théophile-Jules Pelouze (1807-1867) was an outstanding analytical and experimental chemist that worked on a variety of important industrial subjects such as salicine, sugar beet, tannin, pyrogalllic acid, nitrocellulose, butyric fermentation, glass manufacture, and curare. He left us with several analytical and production methods for the above products but little in the way of theory. His works on nitrocellulose were an important element in the development of nitroglycerine production by Alfred Nobel.

LIFE AND CAREER^{1,2}

Théophile-Jules Pelouze (Fig. 1) was born on February 26, 1807, in Valognes, La Manche, Normandie, where his father Edmond Pelouze directed a porcelain industry, built under advise. His father was a very intelligent man that had a very difficult character and for this reason he changed jobs constantly: from Valognes he moved to the Saint-Gobain plate glass factory, then to the Charenton Forges, *Compagnie Anglaise du Gaz*, and other.

There is no information regarding Jules's early education, only that at the age of 16 he took his first work as an apprentice at the pharmacy of Dupuy, in La Fère, and then, in 1825, he continued his training at the pharmacy of Chevalier, professor at the *École de Pharmacie* in Paris. He then applied for a position at the hospital service and was appointed intern at the hospital of *La Salpêtrière*, under the direction of François Magendie (1783-



Fig. 1. Théophile-Jules Pelouze.

1855), a member of the *Académie des Sciences*.

Jean Baptiste André Dumas (1800-1884)¹ tells us that every so often Pelouze would go to visit his father, then working at the Charenton Forges. One day, when returning to Paris on foot after a visit to his family, Jules Pelouze was caught in heavy rain. He hailed a passing carriage that happened to carry Joseph-Louis Gay-Lussac (1778-1856). Gay-Lussac was favorably impressed by the younger man's scientific interest and knowledge and

offered to find him a place in his laboratory.

In 1827 he became an assistant to Gay-Lussac and Joseph-Louis Lassaigne (1800-1859); the latter became famous in connection with the sodium fusion test for the elements. After some time at his laboratory Gay-Lussac proposed Pelouze for a teaching post at Lille where the town council had established a chemistry course to be given by Frédéric Kuhlmann (1803-1881) and there was a vacancy for an assistant. Kuhlmann was a famous chemist that among other things had discovered the catalytic oxidation of ammonia with oxygen to nitric acid in the presence of platinum. Pelouze obtained this post on Gay-Lussac's recommendation and this event marked the beginning of a successful career.

Pelouze worked two years for Kuhlmann and in 1831, after marrying the sixteen-year old daughter of one of his friends (with whom he had one son and three daughters), he returned to Paris to become *répétiteur* in chemistry at the *École Polytechnique*.

Pelouze met Justus von Liebig (1803-1883) when the latter was studying in Paris in 1822 and their subsequent correspondence throws some light on Pelouze's position in Gay-Lussac's Laboratory. In 1832 Pelouze reported that he had prepared and purified specimens of organic compounds recently discovered by Liebig; the specimens were to be used in Gay-Lussac's lectures. Pelouze took special pride in presenting his master with fine samples.

In 1883 Pelouze became assayer to the Mint and in 1836 he spent sometime in Germany, working with Liebig who had established a very successful laboratory in Gießen.

Crosland³ comments that when a vacancy occurred in the chemistry section of *Académie* in 1837, Pelouze expected to count on the powerful support of Gay-Lussac, when running against Pierre-Joseph Pelletier (1788-1842). The latter, however, refused to canvass for his assistant, probably thinking that at thirty he was not yet ready to be elected to such a senior position. The election was held on June 19, 1837; of the 49 members voting 34 did it for Pelouze. Pelletier obtained 15 votes, and Antoine Bussy (1794-1882) and Eugène Melchior Peligot (1811-1890) received 0 votes each (Peligot would later become very famous after discovering strychnine, quinine, brucine, and emetine).

In his subsequent career Pelouze followed very closely in the footsteps of Gay-Lussac, both at the Assay Bureau of the Mint, and finally, after Gay-Lussac's death, as his successor as consultant at Saint-Gobain (1850). While at the Mint, Pelouze developed a titration method for estimating copper, following the precedent established by Gay-Lussac for the estimation of silver.⁴

An associate of Pelouze and a strong candidate for identification with the Gay-Lussac school was Edmé Frémy (1814-1894) who began his chemical training in Gay-Lussac's laboratory at the *École Polytechnique*. It was Frémy whom Gay-Lussac asked to take over his lectures at the *Muséum* in the 1840s. Pelouze and Frémy collaborated in the publication of several textbooks, of which the best known was their *Course of General Chemistry (Cours de Chimie Générale)*, 4 volumes, Paris, 1848-1850.⁵ Following the career of Gay-Lussac and Pelouze, Frémy finally became a consultant at Saint-Gobain.

Pelouze filled many positions and posts. In 1830 he was a professor at the University of Lille; in 1831 he became répétiteur in chemistry at the *École Polytechnique*, where eventually he achieved the position of professor (1831-1846). In 1837 he succeeded Nicolas Deyeux (1745-1837) as a member of the *Académie des Sciences*, and later he succeeded Louis-Jacques Thénard (1777-1857)

in the chair of chemistry in the Collège de France, serving until 1850. In 1833 he joined the *Commission des Monnaies et Médailles* (the French Mint) as assayer and in 1848 became President of the institution, succeeding Engéne Persil (1785-1870). While at the Mint he carried on the recoinage of the silver and copper money. He also represented France in the monetary convention settled between France, Italy, Belgium, and Switzerland.

In 1838 he became *Chevalier de la Légion d'Honneur*; Officer, 12 years later, and in 1854 *Commandeur*. Pelouze received decorations from most countries in Europe and was a member of nearly all the scientific societies.

In 1848 the King of France, Louis-Philippe, was overthrown, the Republic reinstalled, and after the brief bloody war in Paris (the so-called June days), Louis Napoléon Bonaparte was installed as President. Pelouze was a strong supporter of liberal ideas and made them known publicly; he took an active part in the June days as a popular orator and as a combatant. This is probably the reason why in 1849 he was made a member of the Municipal Council of Paris. His activities as a councilman were quite characteristic of a man essentially practical bent –“he was very influential in doing much for the sanitary condition of the great metropolis of Europe; and leaving to his colleagues the charge of the embellishment of the city, he devoted his great knowledge to those important questions on which the health and comfort of the inhabitants depend. He dedicated his efforts to improve the road system, sewers, water supply, street lighting, shelters, and schools. He was untiring in searching out the causes of insalubrities or discomfort, and in finding means for removing them¹.”

Eventually Louis-Napoléon Bonaparte started to lose public respect because of his social and economic measures. In 1851 he managed a successful *a coup d'état* that led to his being crowned Emperor Napoléon III, and instating an authoritarian government. Confronted with these facts Pelouze resigned all his public appointments and devoted all his energies to research and to the direction of the research laboratory he had founded some years previously.

Pelouze had many students but probably the most famous was Claude Bernard (1813-1878). He also

opened his laboratory to the young Marcelin Berthelot (1827-1907) who was soon to collaborate in a study of chemical equilibrium with another of Pelouze's students, Péan de Saint-Gilles. His work with Liebig included investigations on enanthic ether, tannic acid, stearin, sugar, etc., and with Edmé Frémy (1814-1894), Auguste Cahours (1813-1891), and Amédée Gélis (1815-1882), on a series of investigations on vegetable acids, including malic and gallic acids, and on petroleum and butyric fermentation. He was the first to synthesize a fatty substance from glycerin and an acid; to isolate tannic acid; and to make gun-cotton or nitrocellulose in France.

Other work by him was devoted to analytical chemistry and the determination of the atomic weights of several of the elements. Discovering a new class of salts (nitrosulfates) he based thereon a new analytical method for the determination of copper. In 1850 as consulting chemist of the Saint Gobain glass works he introduced sodium sulfate as a constituent in glass-making, producing artificial *aventurine* with chromium as a basis, studying the effect of sunlight on colored glass, and working on enamels.

Pelouze published several books: *Traité de Chimie Générale, Analytique, Industrielle et Agricole* (3 volumes, Paris, 1847), in collaboration with Frémy; *Abrégé de Chimie* (Paris, 1848); *Notions Générales de Chimie* (Paris, 1853).

From his research on saponification, Michel Eugène Chevreul (1786-1889) suggested in his book (*Recherches Chimiques sur les Corps Gras d'Origine Animale*, Paris, 1823) that fats, as neutral bodies, could be considered similar to the ethers of third class (esters) of the Thénard. He described fats as combinations of fatty acids with a substance that added water under the influence of alkali to form glycerin, this substance was analogous to alcohol.

After these first hypotheses, the problem of the constitution of fats (triglycerides) remained unresolved until the first successful synthesis in 1844 of a triglyceride molecule (tributyrin) by Pelouze, in reacting butyric acid with glycerin in the presence of concentrated sulfuric acid and the synthesis of tristearin and tripalmitin by one of his student, Marcelin Berthelot (1827-1907), in 1853 in reacting at 100 °C

fatty acids and glycerin in the presence of gaseous HCl.

In the months of his life, Pelouze was the victim of a series of personal tragedies, first one of his sons in law passed away, followed by the death of his wife and several of his grandchildren. He died in Paris, on 31 May 1867, after an attack of heart dropsy and was buried at the *Cimetière Montmartre* in the family tomb, the corpse being followed by a large *cortège*, composed of all the elite of society, the principal members of the Académie, the Municipal Council, and The National Guard in full uniform. Fremy delivered the funeral oration.

As a suitable final remark we can mention that when Gustave Eiffel built his famous tower in 1889, he decided to honor 72 distinguished French scientists by putting their names in the structure. This 'invocation of science', as Eiffel called it, reflected his worry over accusations that the tower was useless and waste less. There are eighteen names per side of the tower, all positioned just below the first platform of the structure, on the outside. The letters in the names are 60 cm high. Pelouze's name is located on the four *façade*, opposite the view of Paris, next to Carnot's name (Fig. 2).

SCIENTIFIC ACTIVITIES

Some of Pelouze's most relevant contributions to chemistry and chemical technology will be discussed now, with particularly emphasis on those that gave him fame.

Sugar beet

In 1831, after much experimentation, Pelouze published a memoir describing his experiments about beet sugar.⁶ The beet sugar factories located in the Department of the Nord had become very important, but the manufacturers did not have enough knowledge about their raw material and requested Pelouze's help.

After harvesting the beets were first ground and then subjected to a strong pressure that released about two thirds of their weight in the form of a sugary juice. The remaining third was a pulp that was used as animal feed. Pelouze believed that the latter could also be converted almost completely into juice. Jean-Baptiste Biot (1774-1862) had already tried to use the juice for manufacturing sugar, but had suc-

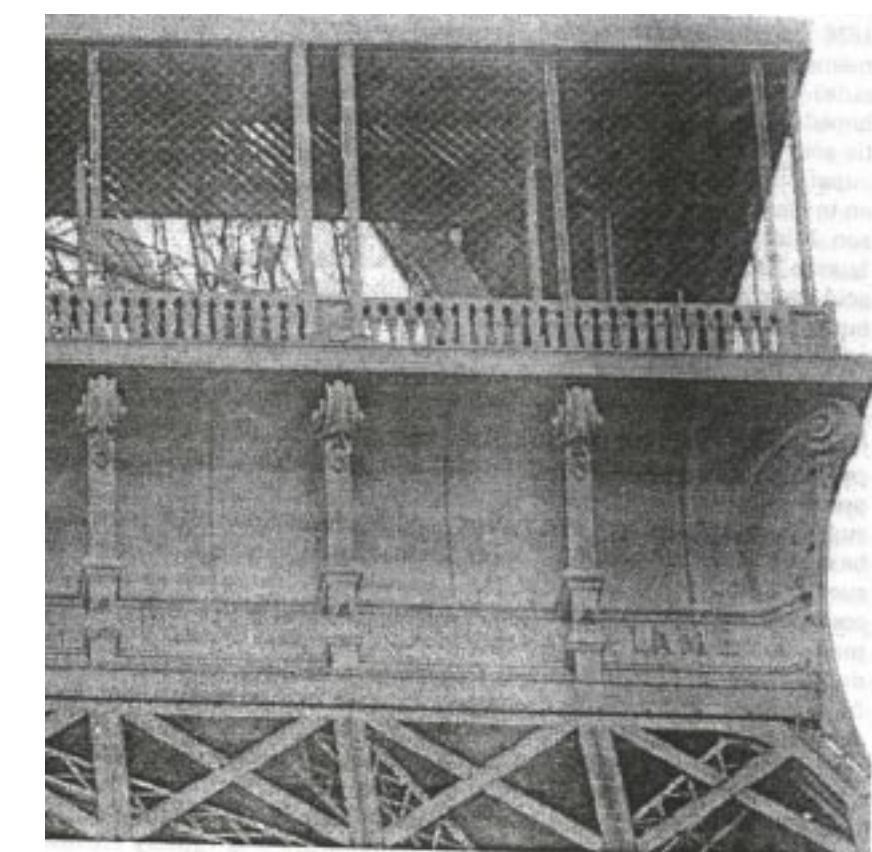


Fig. 2. Pelouze's name in the Eiffel Tower.

ceeded in recovering only one-half of the sugar present in it. Three different sugars were available then: one in the form of a syrup; the second farinaceous, and the third, cane sugar that could be used for manufacturing hard crystals. The last one was the one commercially looked for.

The sugary juice, after concentration, solidified and contained not only the required sugar but also other components that gave it color and helped transforming it into molasses. The question was: were the latter inferior sugars, present in the root or not? Pelouze and his colleague Eugène Melchior Peligot (1811-1890) were able to show that the sugar from the beets was the same as cane sugar, and that the inferior sugars originated from a modification of the primitive sugar during storage of the roots in silos and from the effect of heat on juice. Fresh sugar beet contained only sugar that could be converted completely into candy or loaf sugar, colorless and sonorous. Based on these findings, the local industry modified their manufacturing procedures, cutting the storage time and keeping the roots in a colder place.

Another important contribution of Pelouze was to show that there were two varieties of sugar beet, one containing double the amount of sugar of the other, and that the seeds of the plant did not contain sugar at all. The life of a plant was two years, Pelouze found that sugar accumulated during the first year and that during the second this energy stored was used to create the seed for the following generation.

Pelouze also developed the first analytical procedure to determine the amount of sugar present in sugar beet. His technique was based on fermenting the sugar with beer yeast, measuring the amount of alcohol produced, and comparing it with the amount of alcohol generated by a known weight of pure sugar. According to Pelouze, the procedure was extremely accurate, although it must be remarked that it was also very slow, the fermentation process took fifteen days for completion.

Pelouze first paper was on sugar beet followed later by another one in which he confirmed his original findings and extended them to maize.⁷

Pelouze did some research projects with Jules Gay-Lussac, the

son of Joseph-Louis Gay-Lussac. In 1830 they published a short joint memoir on salicin (saligenin glucoside).⁸ Gay-Lussac had himself hoped to do some research on lactic acid but with many other preoccupations, he passed the research on to his young collaborator and his son Jules. Pelouze and Jules Gay-Lussac had hoped to isolate a new acid from the extract of sugar beet but careful examination of the acid and its salts showed that it was only lactic acid. The resulting paper was competent rather than brilliant and Gay-Lussac senior was happy to publish it.⁹ Pelouze and Gay-Lussac prepared lactic acid by fermenting sugar beet juice at 25 to 30 °C; they believed that during this process sucrose transformed first into glucose and then into mannitol. In this manner, lactic acid could be produced only as very thick syrup, from which it was possible to prepare crystalline lactic acid by sublimation. Elementary analysis of the syrup and of the crystals indicated that the latter corresponded to a dehydrated form of the former. In addition, they investigated the properties of a series of lactates, among them, copper, calcium, zinc, manganese, cobalt, nickel, and aluminium.

Pelouze continued independently his investigations about lactic acid and years later published another paper¹⁰ in which he reported the preparation and properties of several derivatives of the acid, such as lactamide, lactone, and the lactates of iron, copper, ammonium, calcium, magnesium, and zinc.

Prussic acid

Another research area was related to prussic acid (HCN). Pelouze studied the reaction of the anhydrous acid with concentrated hydrogen chloride and with sulfuric acid. His results indicated that the reaction was very exothermic and resulted in the formation of ammonia and formic acid (ammonium formate).¹¹ Heating the ammonium formate to about 180 °C transformed it into water and HCN. Using potassium cyanide instead of HCN resulted in the formation of ammonia and potassium formate. Within this work Pelouze also discovered prussic ether (ethanenitrile), a derivative somewhat less poisonous than prussic acid by the reaction between barium ethyl sulfate and potassium cyanide.¹² Experimentation

with the ether almost cost him his life. Dumas tells us that one evening he was found lying unconscious on the floor of his laboratory, after inhaled too much of the ether.¹

Tannin, gallic, pyrogallol, metagallic and ellagic acids¹³

Another important contribution of Pelouze was the development of an industrial process for manufacturing tannin from gallnuts. Tannin coagulated and precipitated the substance that generated a ferment that made the wines viscous. The product developed by Pelouze became known as Pelouze's tannin.

Pelouze found that a water solution of tannin left in contact with air lost its transparency and yielded mostly gallic acid, in the form of slightly gray crystals, a small amount of ellagic acid. No reaction occurred in the absence of air. Heating gallic acid to about 215 °C generated carbon dioxide and a large amount of white brilliant plates of pyrogallol. If instead, the temperature was rapidly elevated to 250 °C gallic acid decomposed into a large amount of water and a black residue that was insoluble in water that Pelouze designated metagallic acid, having the formula $C_6H_4O_2$.

Enanthic ether and acid

As we have mentioned, Liebig was one of the many people that collaborated with Pelouze. Their collaboration resulted, particularly, on a research published in 1833¹⁴ where they announced the discovery of enanthic ether (methyl heptanoate) and enanthic acid (heptanoic acid). The ether was derived from the distillation of wine broths and had a strong taste and aroma of wine that it communicated to aqueous or alcoholic solutions. This winery aroma was characteristic of the alcohol and also of the bouquet of wines. The ether was decomposed immediately by alkalis into alcohol and enanthic acid. It did not react with alkaline carbonates or ammonia.

Enanthic ether was the first natural ether discovered, it could be linked to fatty materials because of its properties. Eventually Auguste Laurent (1807-1853) produced the ether synthetically from them. Pelouze and Liebig found that a liter of the ether was enough to communicate the particular wine taste and aroma to 200 t of wine.

Butyric fermentation

Alcoholic beverages contain their alcohol from the fermentation of the sugar contained in the mother broths. A second fermentation can take place when the wines are exposed to air. Similarly, fruits or sugar preserves that ferment have simultaneously the odor of alcohol and vinegar.

Pelouze studied very carefully two other types of fermentations: the viscous and the lactic ones. He also discovered and additional one, the butyric fermentation.

In 1814 Chevreul discovered butyric acid in the products of saponification of butter. Pelouze and Gélis reported¹⁵ that although the transformation of milk sugar into lactic acid, in the presence of casein was usually simple and complete, sometimes some complicated reactions were also observed. All the substances that derived from lactic acid had the same composition of the acid, or if they were different, it was because they contained a little or more amount of water. Lactic fermentation could be considered as a simple molecular change, with or without fixation of water, but always without release of gas. Nevertheless, effervescence was observed in some cases, like in alcoholic fermentation, with the remarkable characteristic that hydrogen was observed in the gas released. Pelouze and Gélis indicated that they had found a new fermentation process in which disappearance of sugar was accompanied by the formation of butyric acid. The reaction was not accompanied by a temperature increase and under simple experimental conditions. Production of butyric acid was a true fermentation, similar to that of alcohol and lactic acid it took place by the destruction of a sugar dissolved in water, under the influence of a decomposing animal matter and in the temperature range of 10 to 40 °C. It was possible to use any of the animal substances that yielded the lactic fermentation, but they found that the best were casein and cereal gluten. In order to conduct the reaction properly, it was necessary to do it in a neutral medium and for this purpose sodium bicarbonate was added to the medium. The original reaction mixture was clear and as the reaction advanced it became turbid, and smelled like sour milk. It became so viscous that after some time it was possible to invert the flask without flow out of the charge. The mixture had now

acquired to new characteristics: a large amount of a soft, viscous, rubber-looking substance separated and now lead acetate formed a clear and abundant precipitate. If chalk (calcium carbonate) was present in the original mixture, it remained unchanged during this stage of the reaction.

Afterwards, the viscosity started decreasing, gas began to be released, the chalk dissolved, crystals of calcium lactate, and had the appearance of plaster. Eventually the crystals of calcium lactate redissolved, the liquid became limpid. once again and after some weeks no more gas was released. The liquid contained now calcium butyrate.

Using this procedure Pelouze and Gélis were able to produce batches of 20 to 25 kg of calcium butyrate.

Pelouze and Gélis indicated that the viscous stage always preceded the lactic acid one. Before becoming lactic acid, the sugar went through an intermediate material of global formula $C_{24}H_{10}O_{10}$ that would split into lactic acid.

Butyric acid was easily produced from the calcium salt by hydrolyzing the latter with an aqueous solution of HCl, under boiling conditions. The distillate contained water, butyric acid, and a small quantity of HCl and acetic acid. Treatment of the distillate with calcium chloride caused its separation into liquid phases. Analysis of the acid produced in form yielded the global equation $C_8H_{14}O_3 \cdot H_2O$.

Pelouze and Gélis determined many of the properties of butyric acid: it was a colorless liquid, very mobile, having an odor that reminded of acid and strong butter; its density was 0.963 at 15 °C, and it was totally soluble in water, ethanol, and methanol. It boiled at about 164 °C at atmospheric pressure, and without appreciable decomposition. Its vapor was flammable and burned with a blue flame. It was attacked by sulfuric acid only at high temperatures. They proceeded to prepare a large number of salts (lead, copper, ammonia, magnesium, silver, potassium, barium, calcium, etc.), as well as methyl and ethyl esters.

Glycerin

At Pelouze's time glycerin already known, its chemical role in the structure of fatty materials had been well established by Chevreul.

But its properties were hardly known. Pelouze confirmed Chevreul's hypothesis that oils and fats could be considered as salts having glycerin as the base, he did so by transforming glycerin into a sulfate and phosphate with sulfuric and phosphoric.^{16,17} The products of the reaction were crystalline solids, which were produced with the elimination of water and could be decomposed into glycerin and sulfuric or phosphoric acids through the fixation of water. According to Pelouze, these results confirmed Chevreul's claims that anhydrous glycerin was a component of neutral fats. Pelouze's analysis of glycerin agreed with Chevreul's $C_6H_{16}O_6$ (based on Berzelius's table of atomic weights). In a following work, Pelouze succeeded in combining glycerin with butyric acid to prepare butyrin, reconstituting for the first time a neutral fatty material.

In 1836 Liebig and Pelouze¹⁴ investigated the composition of stearin and derived the formula $C_{146}H_{286}O_{17}$, which could be represented as two molecules of stearic acid, one of glycerin and two molecules of water. If three molecules of water were fixed in the saponification of stearin, then 100 parts of stearin would yield 102.3 parts of products, which 7.9 parts would be glycerin, a result much in accord with those reported by Chevreul.

Of particular interest was the esterification of glycerol with butyric acid, in the presence of hot concentrated sulfuric acid. The fatty material could be saponified by caustic soda producing glycerol and butyric acid. These two results led to the conclusion that the product of the esterification reaction was the same fatty material that Chevreul had discovered in butter, and to which he had given the name butyrin.

Berthelot¹⁸ used Pelouze and Gélis's procedure to esterify glycerin with other acids like acetic, valeric, benzoic, and sebacic. All these esters were oily, slightly soluble in water, had a neutral character and did not react with alkaline carbonates. They could be saponified by alkalis, the reaction was slow and yielded the original acid and glycerin. Acetin (glyceryl triacetate) was the most interesting of the derivatives, it was very soluble in water, had a pleasant odor, similar to that of ethyl acetate, and a sweet sour taste like glycerin.

Cellulose nitrate

Henry Braconnot (1780-1855) had reported in 1833 about the singular product obtained when starch or ligneous materials were treated with nitric acid.¹⁹ The reaction consisted simply in mixing the substance (for example, starch) with several times its weight of nitric acid and after the mixture had dissolved completely adding water to precipitate the product. Braconnot called the new material xyloidine (nitrocellulose), to point that it derived from wood. Although he recognized that xyloidine caught fire easily, he did not realize its extreme detonating properties. He also attempted to make coatings films, and shaped articles from it after finding that the nitrated derivative dissolved easily in wood vinegar. This was an early discovery preceding the work of other scientists with nitrocellulose that led to the advent of plastics and rayon.

In 1838 Pelouze took to study this substance and found that submerging paper, cotton, or linen tissues in cold concentrated nitric acid, produced a parchment that was extremely combustible.²⁰ These discoveries would not have called attention had it not been by the news published in 1846 in political journals, that Christian Friedrich Schönbein (1799-1868, discoverer of ozone) had discovered the transformation of cotton into a powder more powerful than gunpowder. Schönbein improved the production process by submerging the cotton in a mixture of nitric and sulfuric acids and then washing the product to remove the excess acid. Chemists immediately proceeded to relate Schönbein's discovery to the findings of Braconnot and Pelouze.

Pelouze himself reacted to the news by publishing a short historical note in which he recalled the work done by Braconnot and himself and the earlier experiments he had done on the possible detonating properties of xyloidine.^{21,22} In a following publication²³ Pelouze claimed that the material prepared by Braconnot was different from his: xyloidine was the product that water precipitated from a nitric solution of starch while Pelouze's product (which he called *pyroxiline*) was the result of the action of nitric acid on cotton. To justify this claim he gave several examples of the difference between both products, for example, xyloidine dissolved in nitric acid while pyroxiline did not.

Xyloidine was highly flammable and detonated by shock and when distilled in a retort left a considerable residue of carbon; on the other hand, pyroxyline detonated violently when heated to 175-180 °C and was impossible to distill. Pelouze closed his paper with the interesting historical observation that Schönbein had indicated the ballistic properties of gunpowder but kept secret the fabrication procedure, eight years before him Pelouze prepared gunpowder but did not recognize its explosive properties, and Braconnot, first years before Pelouze discovered xyloidine, without understanding its potential.

In the beginning, gunpowder was extolled in excess, criticized extensively, and discarded with indifference. A French-British mixed commission was assigned to test the new material in the Bréa Island. The plan was to compare the effect produced by an underwater explosion of gunpowder and cotton powder on the granite rocks. A fuse, activated by an electrical current, activated the explosions. The gunpowder explosion hardly damaged the rock while that of cotton powder caused the disappearance of a huge rock and reduce it to pieces. No only that, the explosion threw a very large number of deep-dwelling fish to the surface of the sea, either dead or stunned. This surprising result was also used a proof that the mortality of fish that accompanied maritime volcano eruptions was not necessarily due to the heating of the water or to the release of poisonous gases; it could very well be caused by the brusque movement of masses of water.¹

In 1863, Pelouze and Maurey, one of the gunpowder commissars, reported on the use of cotton powder as a war agent.²⁴ The fast explosion of cotton powder that pulverized granite was not considered a menace to the armies, they handled the shock easily. Artillerymen would classify cotton powder in the category of smashing powders which should be kept away from the arsenals. Ordinary powder were different in the sense that cannon powder could catch fire while being prepared as a result of an accidental shock, experience indicated that they did not inflame spontaneously in the storage room. Once prepared, they only danger associated with gunpowder was that resulting from its mishandling. The situation with

cotton powder was different, it could be prepared rather safely but its storage presented a safety risk. No only that, degraded cotton powder would loose its explosive power and would convert in large part to sugary material. At the end of about fourteen years, about one half of the samples exposed to air and humidity would decompose without detonating. Cotton powder remained thus, what from the very beginning a material appropriate for mining more than for military uses.

There are several interesting historical facts associated with pyroxiline. In 1847, Ascanio Sobrero (1812-1888) –an Italian student of Pelouze– discovered a new explosive that he initially called *pyroglycerine* (later known as nitroglycerine). However, Sobrero, both in letters to Pelouze and in a subsequent journal article, issued a warning about the new compound, no only because it had incredible explosive power, but also because it was impossible to handle. During the years 1850-1852, Alfred Nobel (1833-1896) stayed for one year with Pelouze, who had also taught Nikolay Zinin (1812-1880), one of Alfred Nobel's private teachers. It is very possible that all these facts led to Nobel's interest and later occupation with nitroglycerine.

Glass

Pelouze spent fifteen years (1850-1865) as a Director of the Saint-Gobain factory. Many of his technical investigations dealt with the manufacture and properties of glass.²⁵⁻²⁸ He developed an improved process for the manufacture of plate glass, made an exhaustive study of the composition of glass and explained the phenomenon of heat devitrification by the presence of an excess of silica.

It was known that expensive glasses, originally colorless and brilliant, when exposed to daylight would eventually acquire a light or dark violet tint. It was known that these glasses contained manganese. Manganese was added as a "bleach" to glasses that contained iron. When this element was in slightly oxidized the glass remained clear, but further oxidation led to coloring. Not only that, on heating the colored glass returned to the colorless state. It was clear then that under the action of light or heat oxygen would transfer from

manganese to iron, and viceversa. The surprising characteristic was that this transfer took place through the glass, a solid phase, which was almost chemically inert.^{25,28}

Another of Pelouze's contribution was the production of a glass comparable to Venetian *aventurine*. The glass known as aventurine was a Venetian origin and was manufactured in Murano using secret procedures. Eventually, in France, the artisans at the Clichy glass factory were able to discover its production procedure. Venetian aventurine is a yellow glass in which are disseminated a very large number of very small copper crystals. The copper crystals are the result of the reduction of cuprous oxide by ferrous oxide. The resulting ferric oxide gives the yellowish color to the glass while the copper crystals remain disseminated in the mass.

In 1865, Pelouze succeeded in preparing a variation of aventurine glass by adding potassium dichromate to the melt.²⁶ It was known that the sesquioxide of chrome gave a green color to the melts, and particularly to glass. Potassium dichromate had a similar property in producing the sesquioxide of chrome. In enough quantity it gave glass a transparent green color and its crystals remained in suspension in the glass mass. The glass prepared by Pelouze contained 6 to 7 % of chrome oxide of which about one half was combined with the glass and the other half was free in the form of brilliant crystals. Chrome aventurine was harder than pane glass, and particularly more than Venice aventurine; and could be employed for manufacturing jewelry and fantasy items. Pelouze also studied the effect of adding selenium to glass and found that this material imparted it a fine orange tint.

Pelouze also studied the influence of sulfates on the properties of the glasses. It was known that sulfur or alkaline sulfur tinted glass yellow, brown, and even dark black. It was also known that carbon and smoke were used for manufacturing yellow glasses, being introduced in the form of powder coke, graphite, or anthracite. The true source of the color was the sulfur compounds contained as impurities in the carbon. Pelouze performing a series of experiments were he showed that sodium sulfate gave

place to a yellow glass because in the melt it was reduced to sulfide.²⁴

Proust's hypotesis

Among the many subjects that attracted Pelouze's attention was Joseph-Louis Proust's (1754-1826) hypotesis (1815), which stated that the atomic weight of the elements was an exact integer multiple of the atomic weight of hydrogen. Pelouze believed that the very careful measurements of Jean Baptiste André Dumas (1800-1884) of the equivalents weights of carbon, hydrogen, nitrogen, and calcium pointed to a serious error on the generalization of Proust's hypotesis. As a proof of his arguments he proposed using the very simple experiment of taking a well-defined oxygenated compound that was easily decomposed by heat, and weighting it before and after calcinations. In Pelouze's words "l'expérience tout entière consiste uniquement en deux pesées et une calcination."²⁹ To prove his point he used the calcination of potassium chlorate and showed that the equivalent weight of potassium chloride was 74.583 times that of hydrogen and not 74 or 75 times as claimed by others. Pelouze proceeded then to determine the equivalent weight of sodium, potassium, nitrogen, barium, strontium, arsenic, phosphorus, and silicon. In this case his technique consisted of converting the chlorides of the elements into silver chloride, and determining such ratios as $\text{SrCl}_2 : 2\text{Ag}$.³⁰

On the basis of his results Pelouze thought it would be better to use half the atomic weight of hydrogen as the unit of comparison and thus the atomic weight of chloride (35.5 with $\text{H} = 1$), would cease to be an obvious exception.

Curare

In 1844 Pelouze supplied to Claude Bernard a sample of curare and eventually both published a memoir on the subject.³¹ This work was devoted mostly to a description of the physiological effects of the poison after ingestion or injection, on several animals such as birds, rabbits, dogs, and reptiles. Although the action of curare was very similar to that of the venom of a viper, it presented the particular characteristic that after death the nervous system was completely annihilated.

In addition, blood became black, coagulated with difficulty, and did not become brilliant in contact with air. Another peculiarity was that curare added directly to the stomach or the intestinal canal was innocuous and that the loss of toxicity was not due to a chemical reaction with the body fluids. Pelouze and Bernard attributed this result to a characteristic of the mucus gastro intestinal membrane that did not allow the absorption of the poison.

EPILOGUE

Pelouze's results on nitrocellulose have a picturesque angle in Jules Verne's book "From the Earth to the Moon."³² In chapter 9 Barbicane suggests that the problem of reducing the amount of the powder required to produce propulsion can be solved using Pelouze's results: "Nothing is more easy than to reduce this mass to one quarter of its bulk. You know that curious cellular matter which constitutes the elementary tissues of vegetable? This substance is found quite pure in many bodies, especially in cotton, which is nothing more than the down of the seeds of the cotton plant. Now cotton, combined with cold nitric acid, become transformed into a substance eminently insoluble, combustible, and explosive. It was first discovered in 1832, by Henry Braconnot, a French chemist, who called it xyloïdine. In 1838 another Frenchman, Pelouze, investigated its different properties, and finally, in 1846, Schönbein, professor of chemistry at Basel, proposed its employment for purposes of war. This powder, now called pyroxyle, or fulminating cotton, is prepared with great facility by simply plunging cotton for fifteen minutes in nitric acid, then washing it in water, then drying it, and it is ready for use."

"Moreover, pyroxyle is unaltered by moisture -a valuable property to us, inasmuch as it would take several days to charge the cannon. It ignites at 170 degrees in place of 240, and its combustion is so rapid that one may set light to it on the top of the ordinary powder, without the latter having time to ignite."

"Finally, it imparts to projectiles a velocity four times superior to that of gunpowder. So, then in place of 1 600 000 pounds of powder, we shall have but 400 000 pounds of fulminating cotton."

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