# **Antoine Alexandre Brutus Bussy**

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**Abstract.** Antoine Alexandre Brutus Bussy (1794-1882), a French engineer, pharmacist, and physician, out carried important researches in the areas of inorganic and organic chemistry. To him we owe the first exact analysis of alkaloids, particularly morphine and quinidine, an isobaric method for liquefying sulfur dioxide, chlorine, ammonia, and other gases considered to be permanent, the isolation of the elements beryllium and magnesium, a valuable interpretation of adsorption, the discovery of sulfur trioxide, saponin, ricinoleic acid, and the components of the essence of mustard.

**Resumen.** Antoine Alexandre Brutus Bussy (1794-1882), ingeniero, farmacéutico y médico Francés, realizó importantes investigaciones en las áreas de la química inorgánica y orgánica. A él le debemos el primer análisis exacto de los alcaloides, en particular, la morfina y la quinidina, un método isobárico para licuar dióxido de azufre, cloro, amoníaco, y otros gases que eran considerados permanentes, la separación de los elementos berilio y magnesio, una valiosa interpretación de la adsorción, el descubrimiento del trióxido de azufre, de la saponina del ácido ricinoleico y de los componentes de la esencia de mostaza.

#### Life and career

Most of the scarce information available on the life and career of Bussy can be found in the short biography of Picon and in the website of the  $\acute{E}cole$  Polytechnique. <sup>1,2</sup> The following description is taken mainly from these two sources.

Antoine-Alexandre-Brutus Bussy (Figure 1) was born in Marseille (Bouches-du-Rhône) in May 29<sup>th</sup>, 1794, the son of Pierre Bussy and Louise Reynier. He did his high school studies at the *Lycée* de Lyon and at the age of 19. He entered the *École Polytechnique*. Together with his promotion classmates he took part in the defense of Paris against the Allies, after the fall of Napoleon. He fought at Buttes-Chaumont and Vincennes, where he was slightly wounded by the lance of a Cossack. Discouraged by the change in the political regime, he abandoned the career he could have followed as a graduate of the *École Polytechnique* and accepted a position at a pharmacy in Lyon, where he stayed for three years. In 1818, he moved to Paris to continue his studies and took a position at the pharmacy of Félix Henri Boudet (1806-1878) and then moved to that of Pierre-Jean Robiquet (1780-1840), with whom he collaborated in many of his researches, and became director of the laboratory Robiquet had in his factory of chemical and pharmaceutical products.

In 1821, he was appointed *préparateur de chimie* at the *École de Pharmacie* de Paris; in 1823, after graduating as a pharmacist, he was appointed adjunct professor and seven years later (1830) promoted to full professor. In 1844, he assumed the direction of the school (1844-1873), replacing Edme Jean-Baptiste Bouillon-Lagrange (1764-1844). He remained in this position until his retirement in 1873, when he was appointed as *directeur honoraire* of the school. During his administration he was responsible for a fundamental reorganization of the curriculum. He added practical courses to the

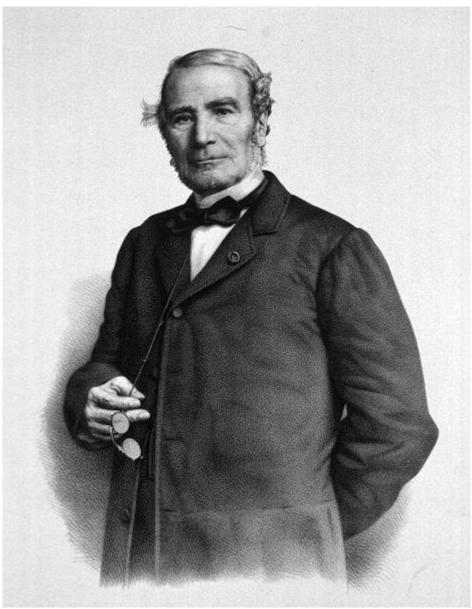


Fig. 1. Antoine Alexandre Brutus Bussy (1794-1882).

theoretical ones, quite a novelty in France at that time, against much opposition from the academic establishment. He was charged by the Assembly of the  $\acute{E}cole$  to present the results of a practical school. The original test was carried out on a cave, with a class of 20 students, split in two years, and selected by competition.

After his retirement, Bussy occupied himself on the plans for building the new *École* at the site of the *Enclos des Chartreux* and also founded at the *École* a laboratory for those young pharmacists who wanted to finish their studies with a thesis, which would be published by the *Journal de Pharmacie*. Unfortunately, he did not live long enough to see the fruits of his efforts: Bussy passed away in Paris on February 1<sup>st</sup>, 1882, at the ripe age of 88. Being a very simple man he requested that no speeches be made at his funeral and no military honors be paid. His wife, children, and grandchildren survived him (this seems to be the only piece of information about Bussy's family<sup>1</sup>).

Bussy possessed an unusual capacity for work. While serving at the *École de Pharmacie*, he taught chemistry at the Athénée de Paris and at the *École de Commerce*, and also begun studies at the *Faculté de Médicine de Paris*, from where he graduated in 1832. His doctoral thesis was about pleurisy<sup>3</sup> and in his teaching thesis he compared the

classification bases of organic and inorganic substances.<sup>4</sup> After graduation he participated in the competition *d'agrégation* (a high-level competitive examination for the recruitment of teachers) at the Faculty and was nominated as substitute of Nicolas Deyeux (1744-1837) in the course of pharmacology. Since the latter was a position limited in time, he abandoned the Faculté de *Médecine* after six years.

In 1824, Bussy was elected member of the *Académie Nationale de Médicine* and became its president in 1856. He was twice elected president of the *Société de Pharmacie* (1836 and 1868). In 1850, he was elected member of the *Académie des Sciences* (académicien libre) replacing Louis Benjamin Francoeur (1773-1849) and in 1856 became *Officier de la Légion d'Honneur*. He was member of the *Conseil d'Hygiène et de Salubrité de la Seine* and of the *Comité Consultatif d'Hygiène Publique* of France, and also one of the founders of the *Union Scientifique des Pharmaciens de France*.

Bussy made important contributions in many areas of inorganic and organic chemistry. He was the first to make the exact analysis of alkaloids, particularly morphine, where he discovered the presence of nitrogen (and amount), a highly debated idea, in his time.<sup>5</sup> In a study about bleaching carbons, he proved that the absorbing power was due to carbon, its surface, and porosity, predicting then concepts that are today accepted without discussion.<sup>6</sup> He was the first to liquefy many gases, such as sulfur dioxide, chlorine, ammonia, cyanogen, and hydrogen sulfide. The result that allowed him to obtain the lowest temperatures known back then.<sup>7,8</sup> The Société de Pharmacie had put a contest on the question if sulfuric acid could exist in the absence of water. He obtained the first prize by discovering sulfuric trioxide. He proved that the manufacture of sulfuric acid in the lead chambers was carried on by the intermediate compound nitrosyl acid sulfate. He was the first to isolate beryllium and magnesium by treating their chlorides with potassium. <sup>10,11</sup> He studied fatty materials, particularly castor oil. 12-16 He elucidated the mechanism of formation of mustard essence, and determined the nature of the compounds that generated it, potassium myronate and myrosine.<sup>17</sup> He resolved the question of the isomeric states of arsenious anhydride and found its antidote, magnesia. 18,19 He studied the fuming sulfuric acid of Nordhausen 9 and the stabilization of hydrogen cyanide and the plaster of wines. <sup>20</sup> He also synthesized and reported the composition of some new double oxalates resulting from the combination of potassium oxalate and the oxalates of ferric oxide, aluminum, and chromium.<sup>21</sup>

#### Scientific contribution

Bussy published about 50 scientific papers about his research and several booklets on medical and public health subjects. As customary of all candidates to the *Académie des Sciences*, he also published a booklet summarizing his researches and findings. Bussel findings.

# Carbon as a bleaching agent

In 1822, Bussy published his first scientific paper, an extensive memoir on the capability of carbon as a bleaching agent.<sup>6</sup> The first part of this publication was a general discussion on coloring matters and bleaching agents. In order to illustrate that the action of a body varied a lot according to its physical state, Bussy gave as example the action of alumina; in the gelatinous state it bleached almost all infusion of dyewoods while it had no action on them when in the dry state. Similarly. The addition of a solution of lead acetate to a liquor removed the color by formation of a precipitate, while the same precipitate in the dry state had no effect at all.<sup>6</sup>

Bussy then discussed the best ways of comparing the bleaching power of different charcoals. He believed that the best procedure was based on using a sulfuric solution of indigo because it was possible to determine exactly the amount of indigo and water it contained, its high sensitivity in changing the intensity of the color, and in being affected very little by light and heat. He used the following procedure to avoid the possibility of the substance being affected by sulfuric acid: He introduced a certainty quantity of wool into a sulfuric solution of indigo; once it had taken all the color it was possible, he withdrew it, washed it with cold water to remove all the loosely adhered dye, and then boiled it in a very dilute aqueous solution of potassium hydroxide to eliminate all traces of the remaining acid. In this manner, he obtained a neutral solution in which the proportion of indigo could be determined using the known fact that 100 parts per weight of chlorine destroyed the color of 220 parts of indigo. In his preparation, the test solution contained 1/1000 weight of indigo.

The bleaching exam consisted on contacting known amounts of the test solution and of the particular charcoal being tested. In his first trials he tried different varieties of charcoal obtained by calcination in a closed vessel, at a temperature sufficiently high to eliminate as much as possible the gases evolved. Calcination of wood, starch, gum, blood, and coal produced a carbon more or less hard, friable and brilliant that *did not sensibly discolor* the test liquor. He then examined bone black and Prussian blue charcoal (obtained by calcining a mixture of animal matter with potassium hydroxide). His results indicated that the bleaching power of the latter was 40 times larger than that of bone black. This impressive difference remained the same even after purifying Prussian blue charcoal by all known methods. Hence, the bleaching power of this type of charcoal developed by virtue of the physical circumstances in which it was placed. 6

Blood and calcined bone yielded a charcoal, which had very low bleaching properties because its particles agglomerated so strongly during calcination that they were unable to combine with the coloring matter. But, for example, if blood was previously mixed with an inert substance, say calcium phosphate, which opposed aggregation, the resulting charcoal had then a bleaching power 12 times larger. Using calcium carbonate increased the bleaching power by 18; using KOH increased it 50 times. The increase was due to a decrease in the size of the resulting charcoal particle and an increase of its porosity. Similar changes in bleaching power were observed when calcining starch, lampblack, potassium acetate, gelatin, and albumen.

Bussy also studied the effect of the coloring matter on the bleaching power by changing the indigo solution by another made of diluted molasses. His results indicated that the same quantity of charcoal bleached about ten times more of the indigo liquor than that of the molasses, and that the different coals kept, in reference to these two substances, the same order in their relative bleaching powder.

It was generally accepted that charcoal acted on coloring matters by decomposition; an assumption based on the observation that when treating different substances with charcoal (e.g. beer, mucilage, molasses, wine, etc.), the discoloration was accompanied by a disengagement of gas. Bussy made some smart experiences to prove that this assumption was wrong and that the gas disengaged was actually gas present in the *original* colored material. Consequently, he concluded that since the coloring matter was not decomposed by bleaching, then it had to attach itself to the charcoal, augment its weight proportionally to the quantity of liquor being discolored, and that under certain circumstances it was possible to recover the solution of the coloring matter.<sup>6</sup>

To test his assumptions, he took five grams of three types of charcoal, which he knew acted with different intensity (blood charcoal, purified bone black, and crude bone black); mixed it with a given amount of diluted molasses, left the mixture in contact for

the same amount of time and then separated the charcoal, washed it dried under the same conditions, and finally weighed the residue. His findings indicated that the original weight of charcoal had increased by 1.56; 0.54, and 0.30 grams, for blood charcoal, purified bone black, and crude bone black, respectively. The same phenomenon took place when using the test solution of indigo, although the increases in weight were smaller.

Bussy concluded that the bleaching property was inherent to coal and that it became evident only when the charcoal occurred under certain physical conditions, among which porosity and particle size were the most important. No charcoal was able to bleach after it had been heated strong enough to become hard and brilliant; it possessed the property only when it was finely divided not by mechanical action but by the interposition of some substances, which opposed particle aggregation. The superiority of animal charcoal was due to its great porosity.<sup>6</sup>

# Liquefaction of gases

In a lecture given to the *Société Philomathique de Paris* on March 13<sup>th</sup>, 1824 Bussy reported a series of observations on the liquefaction of gases. His method of investigation was entirely different from that of Michael Faraday (1791-1867); it was based on the cooling effect produced by a frigorific mixture or the evaporation of liquid sulfur dioxide and not on a change in pressure. Initially, he believed that to achieve the phase change it was necessary to use powerful cooling mixtures, but pretty soon he realized that this was not so, a simple mixture of two parts of ice and one of sodium chloride was enough to liquefy sulfur dioxide.<sup>7</sup> To obtain liquid sulfur dioxide free of water, Bussy passed the gas through a tube full of fragments of fused calcium chloride, and afterwards into a flask surrounded by a mixture of ice and salt, where it completely liquefied and remained in a liquid state under atmospheric pressure at a temperature of 18-20 °C. The liquefied gas was colorless, transparent, and very volatile, and had specific gravity of 1.45. Although it boiled at about -10 °C it could be maintained as a liquid for a long time because the cooling effect produced by its partial evaporation was enough to reduce the temperature to a level much below its boiling point. Poured on the hand it produced an intense cold and completely volatilized. Poured into water at common temperature, one portion dissolved and another volatilized, but as the solution approached saturation, the acid collected in drops at the bottom of the vessel like an oil heavier than water. If in this state it was touched by the extremity of a glass tube, it vaporized, occasioning ebullition and the formation of ice upon the surface of the water. Depending on the relative proportions of water and sulfur dioxide, it was possible to solidify all the water. The bulb of a thermometer enveloped in cotton, dipped into the liquid gas and then exposed to air at 10 °C, fell spontaneously to -57 °C. Under the action of a vacuum pump it was possible to achieve a temperature of -68 °C. These results showed that liquefied sulfur dioxide could be used to solidify many substances, which previously had not been solidified. For example, mercury could be easily frozen with the aid of sulfur dioxide by simply dipping it in the bulb of a mercury thermometer surrounded by cotton and then agitating it in the air. The experiment succeeded better when a bit of mercury was put in a cup together with a small amount of the liquefied gas and the whole subject to the action of a vacuum pump. Through evaporation of the liquefied gas under vacuum, Bussy was able to freeze alcohol of strength below 33<sup>0</sup> (specific gravity below 0.852). The same procedure could also be applied to liquefy other gases, hard to transform into a liquid. It was enough to first dry the gas by passing it over calcium chloride and then through tubes cooled on the outside by the evaporation of sulfur dioxide. Bussy used this procedure to liquefy chlorine, ammonia and cyanogen. In the case of the latter, the cooling effect was strong enough to solidify the compound. In a following lecture given to the *Société de Pharmacie* on March 15<sup>th</sup>, 1824, Bussy repeated the above observations and added that he had been unable to liquefy ether or absolute alcohol using his procedure.<sup>8</sup>

To fully understand the importance of this work of Bussy it must be remembered that Thomas Andrews (1813-1885) would prove the existence of the critical point of a gas almost 40 years later.<sup>31</sup>

# Beryllium

Aquamarine (béril) had been analyzed by Johann Jakob Bindheim (1750-1825) and found to contain 64 % silicon, 27 % aluminum, 8 % calcium carbonate 8 %, and 2 % iron, by weight. René Just Haüy (1743-1822) compared aguamarine with true emerald, found a complete correspondence between their structure, hardness, and density, and come to the conclusion that they were the same material. Hence, he requested from Louis Nicolas Vauquelin (1763-1829) to analyze both materials using chemical methods and see if they contained the same principles and in similar proportions. Vauquelin examined aquamarine and found in it a new earth, which he named terre de béril. 32,33 He first ground the mineral and fused it with potassium hydroxide and found that the resultant mass was totally soluble in aqueous hydrogen chloride. When drying the liquid most of it jellified with the solute retaining a large amount of water. The remaining solid was white and found to be silica. The jellified solution was treated with potassium carbonate and produced a precipitate that previous chemists had assumed was alumina. Vauquelin realized that this was not so because it was only partially soluble in potassium hydroxide. The remaining solid was dissolved in nitric acid, evaporated to dryness, and dissolved again in water, giving a yellow red solution, due to the iron present. The iron was then precipitated by treatment with potassium sulfide. The dissolved residue, treated with potassium carbonate, yielded a white earth that dissolved in acids releasing CO<sub>2</sub>. This residue was the carbonate of the oxide of the new metal. Vauquelin used the carbonate to prepare a number of salts of the new element, and found that all of them had a sweet taste. His first elementary analysis of emerald and beryl showed that their composition was totally different. Emerald contained 64 % silica, 29 % alumina, 2 % calcium carbonate, 3 to 4 % chrome oxide, and about 2 % water. Béril on the other hand, had 69 % silicon oxide, 21 % alumina, 8 % of the new material, and about half percent iron. Additional analytical work carried out by Vauquelin at a later date led him to find that the new material was also present in emerald and that the difference in color between both stones was simply due to the coloring impurities present in each. Vauquelin ended his first memoir with the words "I do not believe that I have to give a definite name to this earth, I will wait until I will know its properties better. Besides, I will be delighted to have the advise of my colleagues". This suggestion was picked immediately by the editors of the Annales de Chimie who proposed calling it glucine, from the Greek  $\gamma \lambda \nu \gamma \nu \zeta =$  sweet, in these words: "The most characteristic property of this earth, confirmed by the latest experiences of our colleague, is forming salts having a sweet taste; we propose naming it glucine, from the Greek,  $\gamma\lambda\nu\chi\nu =$  wine sweet,  $\gamma\lambda\nu\chi\alpha\eta\omega =$  to sweeten". In a logical manner, the corresponding metal would have been called glucinium (symbol Gl) but German scientists substituted its name for beryllium (Be).

In 1808, Humphry Davy (1778-1829) did electrochemical experiments trying to separate the base present in baryta, strontia, magnesia, alumina, silex, zirconia, and glucine. Although he failed in his efforts, he concluded that "from the general tenor of these results, and the comparison between the different series of experiments, there

seems to be very great reason to conclude that alumina, zircone, glucine, and silex are, like the alkaline earths, metallic oxides...Had I been so fortunate as to have obtained certain evidences on this subject, and to have procured the metallic substances I was in search of, I should have proposed for them the names of silicium, alumium, zirconium, and glucium".<sup>34</sup>

Friedrich Wöhler (1800-1882) in Germany and Bussy in France independently achieved the current isolation of the element beryllium in 1828. Wöhler dissolved glucine in ammonium carbonate; mixed it throughly with charcoal and then heated it to redness in a current of dry chlorine gas.<sup>35</sup> The resulting chloride was purified by sublimation as shining colorless needles, and also in a fused mass. According to Wöhler it was very deliquescent and dissolved violently in water disengaging a large amount of heat. He then placed alternate layers of beryllium chloride and flattened pieces of potassium in a platinum crucible, wired the cover on strongly, and heated the mixture with an alcohol lamp. The reaction began immediately and took place with such intensity that the crucible became white-hot. After cooling the crucible, Wöhler added a large amount of water, which resulted in the separation of the beryllium separated out as a gray-black powder. After washing this insoluble metal it was found to consist of metallic particles, which by burning acquired a dark metallic luster. Although Wöhler did not succeed in melting the beryllium, he was able to determine many of its properties. It readily dissolved in sulfuric, clorhidric, and nitric acids; also in a solution of potash yielding hydrogen. Unlike aluminum, it was not acted upon by ammonia: when moderately heated in chlorine, it burned beautifully and sublimed as a crystallized chloride; when heated in bromine vapors, it burned with equal facility, and the bromide of glucinium sublimed in long white needles, fusible, very volatile, and dissolved in water with great heat. Heated in iodine vapors, it burned in the same manner and the iodide obtained sublimed in white needles; in other respects, it was similar to the preceding. It also readily formed compounds with sulfur, selenium, phosphorus, and arsenic.3

In 1827, Wöhler reported that he had been able to separate aluminum from alumina by treating it with chlorine and decomposing the aluminum chloride with potassium.<sup>36</sup> Bussy judged from analogy that glucinium might be separated from its chloride by a similar process; the results proved him correct. He first prepared glucine using Vauquelin's method and after drying it he mixed it with sugar and flour and calcined the mixture. The resulting product, a mixture of glucine and finely divided carbon, was introduced in a porcelain tube and treated with a stream of chlorine. The resulting glucinium chloride deposited at the end of the tube in the form of brilliant white needles. Since it also contained a little of ferric chloride (known to be present in the original glucine), it was purified by distillation in a glass tube. The purified glucinium chloride was then mixed with potassium and heated yielding a mixture of glucinium, potassium oxide, and the remaining glucinium chloride. The last two components were eliminated with water washes, leaving a black residue of glucinium. Bussy studied glucinium chloride and found that it was very deliquescent; when plunged in water it made a noise similar to the one produced by quenching hot iron in water, Beryllium was not attracted by a magnet, it was oxidized with difficult, heated for a long time it converted into a white powder (glucine), which was soluble in acids and precipitated by ammonium bicarbonate. 11

## Magnesium

Magnesium is a metal white as silver and lighter than aluminum that burns with a dazzling brilliancy yielding magnesia. Once again, Bussy believed that Wöhler's

procedure for preparing aluminum<sup>36</sup> could also be use to separate magnesium from magnesia (MgO) by reacting magnesium chloride with potassium. Similarly to aluminum, magnesium had been prepared in very small quantities, highly impure, and inadequate for determining its properties.<sup>11</sup>

According to Bussy, magnesia heated red was not easily attacked by chlorine; to obtain magnesium chloride it was better to use a mixture of the oxide with finely divided carbon. This was easily achieved by following the same procedure used to prepare glucinium chloride: Equal parts of starch and calcined magnesia were mixed with a small quantity of water; the mass divided into small portions and then strongly calcined in a crucible without air contact. The resulting mixture was then introduced into a porcelain tube, heated red and then treated with a stream of chlorine. After some time, the chloride of magnesium melted and flowed along the porcelain tube, solidifying at the end as a white crystalline mass, which when fractured showed large brilliant and slightly flexible plates, looking like spermaceti. The chloride was very soluble in water; had a penetrating bitter taste, and strongly attracted moisture from the air. 11

To reduce the chloride, Bussy used a strong glass tube, about one centimeter interior diameter and about 45 cm long, bent at one end like a retort. He then introduced five or six fragments of potassium, about the size of a pea, both into the bent and the straight pan of the tube, followed by fragments of magnesium chloride, interposed by pieces of porcelain to prevent the chloride from running into one mass by fusion. The potassium section was then heated to vaporize the metal, while the magnesium chloride was simultaneously heated to dull red. The flow of potassium vapors produced a strong ignition, which gradually propagated throughout the tube. After cooling, the tube was found to contain white metallic globules disseminated throughout the chloride that had no decomposed. Cooling and treating with water resulted in the disengagement of hydrogen produced by the small portion of unreacted potassium, accompanied by the formation of white flocks of magnesia derived from the decomposition of a portion of the chloride of magnesium by the potash formed, while brilliant silvery white globules of magnesium precipitated to the bottom of the vessel. The latter were separated from the decanting liquid and repeatedly washed with water. <sup>11</sup>

Bussy proceeded then to study the properties of magnesium. Magnesium metal was found to be very malleable, flattening under the hammer, fusible at a moderate temperature, unalterable in dry air, and losing its metallic splendor in moist air while becoming covered with a white crust of oxide. The latter effect was confined to the surface of the metal. Small portions of magnesium heated in the air burned like iron in oxygen, but larger portions were slowly and difficultly converted into pure magnesia. Pure water, free from air, had no action on magnesium but when boiling it gave out some bubbles of hydrogen. Certain saline substances singularly favored the decomposition of water by magnesium; dilute acid attacked it with the evolution of hydrogen. Magnesium did not amalgamate directly with mercury without the assistance of heat; a very small quantity of magnesium caused mercury to loose its fluidity.<sup>11</sup>

Bussy's procedure allowed the preparation of very small amounts of impure metal, a fact that made difficult the correct determination of its properties. In 1857 Henry Sainte-Claire Deville (1818-1881) and H. Caron returned to Bussy's procedure, except that they used sodium instead of potassium.<sup>37</sup> Reduction of magnesium chloride with sodium in the presence of calcium fluoride as flux produced pure magnesium in yield 75 % of the theoretical. Their method allowed them to prepare a large amount of magnesium, which they purified by distillation in carbon vessels in a hydrogen atmosphere. Afterwards, they made a detailed study of its properties. Magnesium was found to be volatile as zinc at more or less the same temperatures; sublimation of the

pure metal did not leave any residue and the sublimed material was white and surrounded by a small amount of oxide. When the metal was impure, sublimation left in the carbon vessel a very light black residue of complex nature, and the distilled magnesium was covered by small transparent needles, very unstable, and decomposing very rapidly into magnesia and ammonia. The latter fact suggested the presence of a nitride. Pure magnesium melted at a temperature close to the melting point of zinc. At a slightly higher temperature it caught fire producing a brilliant flame.

# Sulfuric acid

Sulfuric acid of Saxes was the acid obtained at Saxes (Nordhausen) by distillation of iron sulfate. For a long time this was the only procedure for manufacturing sulfuric acid until the method of the lead chambers came into being and became the largest European source of the acid. Since the Saxes acid possessed certain valuable properties that made them particularly useful for certain technologies, the *Société de Pharmacie* established a prize-contest for the best answer to the questions (a) the true nature of the sulfuric acid from Nordhausen, (b) the action of heat on iron sulfate and other sulfates decomposable by caloric, (c) and a method for preparing the Saxes fuming sulfuric acid. Bussy participated in the contest and his memoir got the first prize.

According to Bussy,<sup>22</sup> the Saxes sulfuric acid available in commerce was a brown liquid of variable density, but differing very little from the ordinary sulfuric acid. It had a strong sulfurous smell when and in contact with air it released very suffocating vapors. When heating it started boiling at about 40-50 °C; little by little a part evaporated as very thick vapor, and after a short while it ceased to boil unless the temperature was increased substantially. At this stage the original brown color had disappeared and the residue behaved exactly like ordinary sulfuric acid. Since the simple action of heat converted the Saxes acid into ordinary acid, it was logical to assume that the former owed its properties to the substance that was released by heating. Hence, Bussy decided to distill Saxe's acid without contact with air and to collect the emerging vapors by submerging the receiving end of the retort in ice. He heated the flask slowly and collected the distillate in the cooled recipient, where it soon transformed into a solid (concrete) mass. This distillate was found to have the following properties: It was a white opaque solid, hard to cut, and releasing vapors at room temperature. Left in contact with air it absorbed humidity and slowly transformed into a dense liquid similar to sulfuric acid. Contacted with vegetable substances, such as paper and wood, it carbonized them promptly. When poured into water it sizzled strongly and the resulting aqueous solution had all the properties of diluted sulfuric acid. The addition of a small amount of water resulted in the release of heat and vapor but not in the production of gas. All these properties seemed to indicate that the substance being examined was solid (concrete) sulfuric acid (sulfuric trioxide, melting at 290 K and boiling at 318 K).<sup>22</sup>

In order to assure that water did not cause the formation of sulfuric acid, Bussy treated the solid sulfuric acid directly with different bases, for example, barium hydroxide. Again, a strong reaction took place with no release of gas. The resulting solid, which looked like barium sulfate, was treated with HCl and no release of  $SO_2$  or hydrogen sulfide took place. Measurement of the weight of the different reagents proved that the solid sulfuric acid contained no water, in other words, it was anhydrous sulfuric acid. Bussy found that this material could exist both in the liquid and solid state. When liquid, it was more fluid than the ordinary sulfuric acid; it strongly refracted light and had specific gravity of 1.97 at about  $20^{0}$ C.

Bussy concluded that the Nordhausen sulfuric acid should be considered as ordinary sulfuric acid, which contained in solution a certain amount of anhydrous sulfuric acid. This solute was the source of its particular properties. The brown color and the sulfurous odor were not essential properties; the first factor originated most probably from the accidental presence of animal or vegetable substances; the second, from a small amount of sulfur dioxide dissolved, which originated during the production process. Bussy remarked that in 1812 Augustus Vogel (1817-1889) had postulated, without offering any experimental proof, that fuming sulfuric acid was ordinary sulfuric acid, which an imponderable factor had transformed into a higher state of acidity. According to Bussy, the available experimental data supported his explanation that concrete sulfuric acid was anhydrous sulfuric acid.<sup>22</sup>

Bussy went on to study the decomposition of ferrous sulfate and its hydrate by heat. Initially the hydrate lost its water of hydration and left as a residue the anhydrous salt. Further heating led to the release of sulfur dioxide, followed by release of oxygen. Analysis of the final mixture of gases showed that it contained two parts of sulfuric acid (sulfur trioxide) and one of oxygen. Absorption of the mixture in water indicated the formation of sulfuric acid. The remaining solid residue was found to be ferric oxide. According to Bussy, these results suggested that at the beginning of the calcination part of the sulfuric acid decomposed under the influence of ferrous oxide into sulfur dioxide and oxygen, while the iron went into its maximum degree of oxidation. Once this point had been reached, part of the sulfuric acid volatilized without decomposition and dissolved in the water while the remaining was decomposed by heat into two volumes of sulfur dioxide and one of oxygen.

Similar results were obtained from heating other sulfates such as those of copper, zinc and antimony, as well as alum (hydrated potassium aluminum sulfate). In other words, sulfur trioxide was one of the common products of the distillation in a closed vessel of a sulfate decomposable by heat. Bussy reported that one particularly interesting property of liquid sulfuric trioxide was that it dissolved indigo immediately, producing a beautiful purple red solution instead of the blue one obtained with ordinary sulfuric acid. Bussy proved that this phenomenon did not take place with sulfur dioxide. The red solution, put in contact with humid air converted into a blue one because the water absorbed converted the acid into ordinary sulfuric acid.<sup>22</sup>

Bussy went on to study the manufacture of Saxe fuming sulfuric acid, using his findings that Nordhausen sulfuric acid differed from ordinary sulfuric acid in containing a higher concentration of acid and that the anhydrous acid (sulfur trioxide) could be obtained by the distillation of iron sulfate. An adequate collection of the products from the latter's distillation would allow manufacturing sulfuric acid of any desired concentration. His final conclusions were the following: (a) the Nordhausen sulfuric acid was ordinary sulfuric acid containing a certain amount of anhydrous sulfuric acid. The latter provided the characteristic properties of this acid, (b) the anhydrous acid could be separated by distillation and one of its many remarkable properties was that it dissolved indigo yielding a red solution, (c) all sulfates decomposable by heat yielded oxygen, sulfur dioxide, and sulfur trioxide, which was essentially characterized by the white vapors produced during the decomposition, and (d) all sulfates could be used to prepare ordinary sulfuric acid and fuming sulfuric acid, by the procedure he described.<sup>22</sup>

Desormes and Clément had been the first to propose a rational theory for the homogeneous catalytic effect of nitrogen oxides in the lead chamber process for the manufacture of sulfuric acid.<sup>38</sup> They did so by establishing for the first time a quantitative relation between the sulfur dioxide, oxygen, and oxides of nitrogen that participated in the process. They were certain that the combustion generated a mixture

of NO, SO<sub>2</sub>, water vapor, and nitrogen from the air, and probably the part of the oxygen that had escaped the action of sulfur. Their experiences indicated that NO and SO<sub>2</sub> could not coexist together without reacting. The lower temperature existing downstream the lead chamber resulted in condensation of part of the vapor; the resulting mist contained the sulfuric acid generated, and offered a very large number of contact points that increased the conversion to acid. After the production of the first amount of sulfur trioxide, the remaining gas mixture was composed of NO, sulfur dioxide, and residual air containing less oxygen. The NO would necessarily convert into nitrogen dioxide, which would then decompose again reacting with a second portion of sulfur dioxide, until all of this oxide or the atmospheric oxygen became exhausted. After the sulfur dioxide had been converted totally into trioxide, the remaining gas was composed mainly of a large amount of nitrogen and nitrogen oxides. Hence, it was clear that nitric oxide was only the *instrument* for the total oxidation of sulfur; it was its base, NO, that took the oxygen from the atmospheric air and transferred it to SO<sub>2</sub>, time after time.<sup>38</sup>

Desormes and Clément's experiments revealed that the reaction between  $NO_2$  and  $SO_2$  was a series reaction, the two gases first forming a compound, observed as crystals, which was then decomposed by water. Their explanation may be considered the first in which an intermediate compound is assumed to play a part in a catalytic reaction.

To prove their point, Desormes and Clément simulated the process taking place in the lead chamber by feeding into a glass vessel a mixture of sulfur dioxide, air, and a small quantity of nitric oxide (about 5 % of the weight of SO<sub>2</sub>) and noting that "the oxide grows red (forming NO<sub>2</sub>), and spread itself throughout the space; then clouds of white fumes roll across the vessel, and deposit themselves on the walls in shinning, stellated crystals. These thick whirls of sulfuric acid were succeeded by clearness; and if at that moment a little water was added, the crystals of acid dissolved with great heat, and the nitrous oxide gas, again becoming free, changed once more into the red acid, and the same phenomena began anew until all the atmospheric oxygen was used up, or all the sulfurous acid burned. The remaining gases are just as we indicated in our conjectures; for the color of the nitrous acid appears with almost all its initial intensity; after the complete operation there is no more odor of sulfurous acid, but much nitrogen, and only sulfuric acid on the walls of the vessel. If during the combustion of SO<sub>2</sub> there is a large contact between the added water and the gas, due to intensive mixing or the presence of a large amount of water, then the reaction becomes slower and incomplete because liquid nitric acid is formed; the latter has little action upon the gas being burned".

Desormes and Clément closed their paper with the statement that "this experience leaves no doubt regarding the theory of fabrication of sulfuric acid, which is only a simple exposition of the facts...This theory offers us the means to improve our knowledge about the proportion of the elements of sulfur dioxide and sulfuric acid; it gives us the hope of finding the same mode of action in other chemical operations illunderstood..." <sup>38</sup>

In a following publication Bussy <sup>9</sup> summarized the findings of Desormes and Clément and those of Gay-Lussac. Gay-Lussac's opinion was not generally accepted because of the uncertainty prevalent at the time about the composition of the different compounds of nitrogen. For this reason, Bussy decided to investigate further the question of nitrogen compounds.

According to Gay-Lussac, there were five well-defined combinations of nitrogen with oxygen, in which two volumes of nitrogen were combined with one  $(N_2O)$ , two  $(NO_2)$ , three  $(N_2O_3)$ , four  $(N_2O_4)$ , and five  $(N_2O_5)$  volumes of oxygen.<sup>39</sup> The first two were named nitrogen protoxide and nitrogen deutoxide (and some times nitrous gas). The

fifth one corresponded to nitric acid deprived of water. The composition and names of the third and fourth combinations were not so clear. The fourth one had been named nitrous vapor and nitrous acid; it was obtained from the direct combination of two volumes of nitrogen deutoxide with one volume of oxygen, or by combining at low temperature (-18 to -20 °C) the products of the decomposition of anhydrous lead nitrate. The third combination was called hyponitrous acid and resulted from the combination of four volumes of nitrogen deutoxide with one volume of oxygen. Dalton was of the opinion that the numerous combinations obtained by contacting oxygen with different amounts of nitrogen deutoxide were simply nitric acid combined with hyponitrous acid in different proportion. Berzelius adopted Dalton's opinion. Consequently, Bussy believed that these new opinions required changing the nomenclature of the oxides of nitrogen in order to bring them into line with that of analog compounds. Hence, he proposed that hyponitrous acid might be simply named nitrous acid, because its composition was similar to that of phosphorus and arsenious acids, and similarly, (old) nitrous acid should be named hyponitric acid because of its similarity with hypophosphoric acid.<sup>9</sup>

Desormes and Clément's theory was later improved on the basis of more exact knowledge about the combinations of nitrogen with oxygen. Their theory, although basically correct and leading to the expected result, did not give a satisfactory explanation of all the details of the phenomenon. For example, Gay-Lussac had shown that the crystals reported by Desormes and Clément also decomposed by water in an atmosphere of carbon dioxide, forming red vapors. This result was inconsistent with the assumption that they only contained sulfur trioxide and nitrogen deutoxide because the latter did not form red vapors in contact with carbon dioxide. According to Gay-Lussac, the crystals were actually composed of per-nitrous (nitrous) acid and sulfuric acid (sulfur trioxide). The latter supposition was confirmed by the fact that it was possible to directly produce the crystals by pouring into sulfuric acid the product of the distillation of anhydrous lead nitrate.

According to Bussy, the conflicting evidence about the true nature of the crystals required additional experiences. His experiment consisted on filling a graduated flask with concentrated sulfuric acid and flowing through it a stream of nitrogen deutoxide followed by a stream of oxygen. On contact, the red coloration appeared accompanied by the formation of crystals observed by Desormes-Clément. The crystals dissolved in sulfuric acid as their concentration increased and condensation of the gas mixture. Thus, under the influence of sulfuric acid, nitrogen deutoxide and oxygen combined to form nitrous acid. According to Bussy, the crystals were formed by the combination of sulfuric acid and nitrous acid. 9

Based on the result of his experiments, Bussy formulated a new theory for the formation of sulfuric acids, which satisfied all the experimental findings: Mixing sulfuric dioxide with oxygen and nitrogen deutoxide humid, resulted in the immediate formation of hyponitric acid, which released part of its oxygen to sulfur dioxide, converting it into sulfur trioxide. The latter combined with nitrous acid to form the compound with sulfur that united with water to generate the crystalline deposit. The crystals, treated with water, ceded the sulfur trioxide to the solvent, and the remaining nitrous acid (which could not exist in the free state) transformed into nitrogen deutoxide (which became red in contact with oxygen) and hyponitric acid, equally red. Thus, when the experiment was done in an atmosphere of carbon dioxide, red vapors were generated, as reported by Gay-Lussac, because of the hyponitric acid generated. The hyponitric acid reacted again with sulfur dioxide, repeating the chain of events observed during the manufacture of sulfuric acid.

## Fatty materials

Bussy, alone or in collaboration with Louis René Lecanu (1800-1871), made a detailed study of the distillation of fatty materials, particularly castor oil, <sup>12,13,40</sup> the reaction of fatty acids with nitric acid, and the properties of fatty acids such as ricinoleic, elaiodic, margaric, and suberic. <sup>14,15,41</sup>

Michele Chevreul (1786-1889) had extensively studied the preparation and properties of animal and vegetable fatty materials,<sup>42</sup> although he had not looked into the nature of the products formed during their distillation. It was assumed that the distillation of fatty materials yielded water, acetic acid, methane, carbon dioxide, and a particular acid that Louis-Jacques Thenard (1777-1857) had designated as sebacic acid.<sup>43</sup> It was also known that distillation also passed a large amount of fatty material, sometimes liquid, sometimes solid, of unknown identity and composition.

In order to clarify the matter, Bussy and Lecanu distilled a large number of fatty materials of animal and vegetable nature (e.g. tallow, pork fat, oil of olives, poppy seeds, bitter almonds, linseed, etc.) and observed a very similar behavior. The process itself was characterized by three stages. Once ebullition started, oleic acid and margaric acids were formed in addition to gaseous products. Afterwards, it passed an empyreumatic oil which did not contain fatty acids, and finally, when all the distillates have passed, a yellow red substance sublimed. Although the proportion of these substances varied according to the nature of the raw material being distilled, the general characteristics of the process were the same. For example, when heating poppy seed oil, at about 200 °C it deposited a mucilaginous substance and became colorless. Once it started boiling, gases were released, the oil achieved a strong penetrating odor, and then began distilling without becoming colored. The first distillate (about one third of the initial mass) was a liquid that on cooling turned into a soft solid; afterwards the odor disappeared and the rest of the charge passed over as a liquid and left in the flask a carbonaceous residue. Examination of the gas disengaged at the beginning of the operation showed it was composed of flammable gases mixed with methane, carbon monoxide, and carbon dioxide. The first liquid fraction became solid at about 20 °C; it was yellow and very odorant, dissolved completely in alcohol, reddened litmus, and most of it combined with an aqueous solution of KOH forming a real soap. According to Bussy and Lecanu, it could be considered a mixture of acetic, sebacic, oleic, and margaric acids, an empyreumatic oil, and a smelly oil; that is, it was quite similar to the product that Chevreul had found when distilling stearin and olein. Treated with boiling water, it yielded a white solid flocculent matter, which could be separated by filtration and shown to be sebacic acid. The semi-solid mass remaining after treatment with boiling water, pressed between sheets of papers, provided a compact colorless pearly mass, melting at 57 °C, which proved to be margaric acid (then palmitic acid, today heptadecanoic acid). The liquid that passed the paper pressing stage was shown to contain oleic acid.

The remaining distillation fractions were analyzed and not found to contain substances of particular interest.

Bussy and Lecanu ended their memoir indicating that the distillation of the other fatty materials studied followed the same stages, the only difference being the relative amounts of the different products obtained.<sup>12</sup>

In a following publication on the subject,<sup>14</sup> they extended the experiments to fatty materials not formed by stearin and olein, that were, spermaceti, ethal (cetylic alcohol), and the crystalline mater of gallstones (*cholésterine* = cholesterol). Chevreul had reported that spermaceti was a substance hardly attacked by alkalis, which on long

contact transformed into oleic acid, margaric acid, and a fatty material quite different from glycerin, which he had named *éthal*. Bussy and Lecanu found that distillation of crude spermaceti provided the following substances: spermaceti, a colorless oil, acids oleic, margaric, and acetic acids, water, odorous substance, a yellow material, and a yellow empyreumatic oil. Similarly, cholésterine and éthal were shown to distill without producing fatty acids.

In another publication about fatty materials, Bussy described the results of his study on the action of alkali on fatty materials at high temperatures.<sup>44</sup> He had already found that the distillation of animal fatty materials produced a mixture of oleic and margaric acids, plus other pyrogenic substances. The results of this process were substantially different when the fatty materials were heated with calcium hydroxide, barite, strontium oxide, or the hydroxides of potassium and sodium. For example, distillation of a mixture of 100 parts of tallow with 50 parts of calcium oxide passed a liquid, which solidified on cooling. Pressing it between two pieces of paper resulted in the absorption of a yellow empyreumatic material and the separation of pearly brilliant solid, which externally looked like margaric acid, but did not have the required physical properties; for example, it was not acidic and could not be saponified with hot or cold alkali. Chevreul had already shown that alkali transformed fatty materials in completely different substances; hence it seemed logical to assume that the same phenomenon took place when distilling the above mixtures. The new substances found were the result of secondary reactions between the alkali and the acids produced by the hydrolytic process. In order to test this hypothesis, Bussy studied the distillation of binary mixtures of alkali with the acids margaric, stearic, and oleic.

Distillation of a mixture of highly purified margaric acid and calcium (or calcium margarate) yielded a soft mass, which was pressure filtered between two pieces of paper and then purified by successive washes of boiling alcohol until its melting point remained still at 77 °C. The distillation residue contained calcium carbonate and other products. The purified material was found to be partially soluble in ether and in ethyl acetate and not to react with a boiling concentrated solution of potassium hydroxide. An approximate elemental analysis showed that its composition was similar to that of a hydrocarbon, although it contained a small amount of oxygen. Bussy believed that it was the result of a reaction in which margaric lost one molecule of carbon dioxide; he named the new substance *margarone* (today we now that margarone is the ketone of margaric acid).<sup>44</sup>

A similar treatment of the mixture stearic (or oleic) acid + calcium oxide, yielded similar results, which again were assumed to be the result of a reaction in which stearic (oleic) acid lost one mole of carbon dioxide. This new substance was named *stearone* (oleone). Bussy believed that margarone and stearone could be used to manufacture high-price candles.<sup>44</sup>

Distillation of castor oil showed that this fatty material behaved different from other vegetable oils. In addition to the usual gas phase, it could be separated into water, acetic acid, a volatile oil, a solid fatty acid (ricinic acid, today ricinoleic acid) a liquid fatty acid (elaiodic acid), and a solid residue remaining in the retort. A remarkable feature of the distillation was that when the temperature reached about 270  $^{0}$ C, the oil split into two phases, a liquid one containing water, the acids ricinic and elaiodic, and an essential oil; the second phase was spongy, colorless, and had a consistency similar to soft bread. <sup>16</sup>

Bussy and Lecanu described ricinic acid as a white pearly color solid, having a very acrid taste, melting at about 22  $^{0}$ C, insoluble in water but soluble in alcohol and ether, and that the latter solutions strongly reddened blue litmus. It was dissolved by alkalis

forming a kind of soap, soluble in water and alcohol and decomposable by earth salts. The sodium and potassium salts were soluble in water and alcohol, the calcium, magnesium, and lead salts were insoluble in water and very soluble in alcohol. Elaiodic acid was a yellow colored oil, having a sharp taste, a slight empyreumatic smell, solidifying at several degrees below 0 °C, and dissolving easily in alcohol, ether, and alkaline water. It combined very easily with bases; the potassium and sodium salts dissolved readily in water and alcohol while the magnesium and lead salts were insoluble in water and easily soluble in alcohol, The solid residue of the distillation was of yellow white color, full of cavities, and somewhat resembling the crumbs of fresh bread. It was insoluble in water, alcohol and ether but dissolved in alkalis forming a kind of soap. It did not decompose at high temperature, inflamed when exposed to an ignited body, and burnt readily without melting.

Another interesting observation was that when instead of distilling castor oil it was treated with a solution of KOH or NaOH, it saponified even more easily than olive oil, forming the corresponding ricinate, elaiodate, and margaritate, and glycerin. These salts were very soluble in water and behaved like regular soaps. <sup>16</sup>

In a following paper, Bussy studied the essential oil that separated when castor oil was heated to about 270  $^{0}$ C, and which he then named cenanthol.  $^{40}$  A second distillation of this material yielded a volatile yellow oil and a residue composed of water and ricinic and elaiodic acids. True cenanthol (heptanal today) was colorless and had a strong aromatic odor; it strongly refracted light, its density was 0.8271 at 7  $^{0}$ C, it dissolved completely in alcohol and ether, and boiled between 155 and 158  $^{0}$ C. An elemental analysis yielded a composition corresponding to the formula  $C_7H_{14}O$  (based on two volumes of vapor). Cenanthol, in contact with humid air, crystallized as its hydrate. It was not attacked by potassium hydroxide but nitric acid or chromic acid oxidized it to cenanthylic acid. Alexander William Williamson (1824-1904) further investigated this substance and found that although its composition was as reported by Bussy, it reacted with very concentrated potassium hydroxide yielding the corresponding cenanthylate and another oil more carbonated than cenanthol. Bubbling chlorine through an alcoholic solution of cenanthol produced the ether,  $C_9H_{18}O_2$ , and other products.

## Saponin

In 1832, Bussy was asked by the *Société d'Encouragement* to examine the root of the plant saponaria of Egypt as a possible substitute for soap. The root was considered to belong to the *Gypsophila struthium*, a plant, which grows spontaneously in Hungary, Greece, and many countries of the East. Bussy indicated that the dry pulverized root acted as a powerful sternutatory; dissolved in water it yielded an unctuous solution that upon agitation it foamed the same as a soap solution and easily cleansed tissues. In order to isolate the active principle Bussy first treated the powdered root with ether and concentrated the extract by evaporation until it remained as a sticky red substance, which weakly reddened litmus. Treatment with cold alcohol separated it into two parts, one white, insoluble in the solvent, and another red, soluble in alcohol. The portion insoluble in cold alcohol was dissolved in hot alcohol and after cooling it yielded a fatty material having the characteristics of stearin. The portion soluble in hot alcohol was composed of a fatty material accompanied by a red resinous substance.<sup>47</sup>

The residue of the ethereal extraction was then treated with boiling alcohol of 36<sup>0</sup> (density 0.837); after cooling it deposited a white flocculent substance looking like stearin but more gelatinous. The residual root was found to have lost its acrid flavor, the sternutatory property, and the capability of foaming in water. All these properties were

found to be present in the substance extracted by boiling alcohol, which Bussy named *saponin* to reflect its foaming ability. The material was obtained in a more pure form by digesting the powdered root in boiling alcohol of 36<sup>0</sup>, followed by filtration through a cloth and cooling. The procedure was repeated until the root was exhausted. The resulting saponin was white, non crystallizable, and friable. It had an acrid and sharp taste, which remained for a long time in the mouth. In powder form, it acted as a powerful sternutatory. Saponin was soluble in water in all proportions; the solution frothed strongly even when it contained only 1/1000 weight of saponin. It was soluble in alcohol of all concentrations but the solubility decreased as the concentration of alcohol increased. It was insoluble in ether and burned in air producing an aromatic smell. When distilled it blackened, swelled, and gave off an acid empyreumatic oil. According to Busy, saponin was not affected by dilute acids but was decomposed by boiling nitric acid into a yellow resin, and mucic, and oxalic acids. Similarly, it was not affected by diluted alkalis. All these properties suggested classifying saponin in a category near gums, particularly due to the fact that it contained mucic acid.<sup>47</sup>

## Mustard seeds

Robiquet, in collaboration with Antoine François Boutron-Charlard (1796-1879), had proven that water played a critical role in the formation of the principles of white mustard, that the composition of the seeds of white and black pepper was essentially different and that the active principle of the seeds of white mustard resided in a non volatile substance that did not preexist in the seeds. This substance was probably a derivative of sinapisin, which contained sulfur. The active principle of the seeds of black mustard was also a volatile oil that did not preexist and developed in the presence of water. Sinapisin extracted with alcohol, in the absence of water, was unable of coloring red with ferric salts or developing odor in the presence of caustic alkali. Sulfur was present in a large amount, probably as sulfur hydrocarbon (eventually allyl sevenol, allyl thyocianate, would be identified).

Robiquet, in collaboration with Bussy, continued investigating the volatile oil of mustard,<sup>49</sup> but it was left to Bussy to isolate the active component of the mustard's essence. In a paper published in 1839,<sup>17</sup> he reported finding in the flour of grey mustard two components that reacted in the presence of water to yield the essential oil. One was a new acid, which he named *myronic* acid (from the Greek  $\mu\nu\rho\nu$  = essence); the other was very similar to albumin, and hence named myrosyne (from the Greek  $\mu\nu\rho\nu$  = essence and  $\sigma \upsilon v = \text{with}$ ). Myronic acid was odorless and was present in grey mustard as potassium myronate (sinigrin), C<sub>10</sub>H<sub>16</sub>KNO<sub>9</sub>S<sub>2</sub>, a colorless, odorless bitter salt, completely soluble in water. Myrosyne was a substance soluble in water, coagulable like albumin by heat, acids, and alcohol. When put in contact with potassium myronate it developed the smell of mustard and the distillation of the resulting liquor delivered the essential oil. Myrosyne existed in black mustard simultaneously with myrosyne and released mustard smell when adding cold water to a powder of the seed. This phenomenon did not take place when the cold water was replaced by hot water, alcohol, or slightly acidic water. Yellow mustard was found to contain myrosyne but not potassium myronate; hence it did not smell when treated with water. The pertinent aroma developed if the latter solution was treated with a solution of black mustard in alcohol.17

## Wine making

In 1854, Chancel formed part of a committee appointed by the Chamber of Commerce of Montpellier to study the question of plastering of wines. The conclusions

became public in 1865 and were partly published in *Comptes Rendus*.<sup>20</sup> The work reported by Antoine Bussy (1794-1882) and Henri Buignet (1815-1876) related to the study of the possible reactions that might take place between the foreign substance, calcium sulfate, and cream of tartar, in an alcoholic medium. For this purpose, they prepared a synthetic solution with the three ingredients and studied its behavior and properties. They found that addition of calcium sulfate decomposed the cream of tartar without changing the initial acidity of the solution of cream of tartar in alcohol. The reaction took place between one equivalent of each of the two salts. If an excess of sulfate was added, it remained in solution unaltered, or it precipitated. The sulfate reacted totally, the calcium becoming neutral calcium tartrate, of which the largest part precipitated. The sulfuric acid released became part of the solution, apparently as potassium bisulfate.

Bussy also published an extensive report on the use of the thermometer of Conaty (an instrument indicating the alcohol content of a wine but its boiling point) and the dilatometer of Johann Theobald Silbermann (1806-1865) for detecting the purity of wine (and hence its possible fraud).<sup>50</sup>

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