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Edmund frémy

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RESUMEN Edmund Frémy (1814-1894) desarrolló un amplio conjunto de investigaciones en química inorgánica y orgánica; caracterizó los ácidos férricos, estáñonnico, antimónico, y osmico; realizó la síntesis de rubíes y de vidrio de color; preparó un gran número de fluoruros, aisló el ácido fluorhídrico, y demostró que era un hidrácido; estudió la preparación y propiedades del ozono, e investigó la constitución de las plantas y la fisiología vegetal. Descubrió e identificó el ácido palmítico en el aceite de palma y sintetizó la sal de Frémy, un radical libre de larga vida usado como estándar en la espectroscopia de resonancia paramagnética.

ABSTRACT Edmund Frémy (1814-1894) carried extensive research in inorganic and organic chemistry; he characterized ferric, stannic, antimony, and osmium acids; synthesized artificial rubies and colored glasses; prepared a large number of fluorides, isolated fluorhydric acid and proved it was an hydroacid, studied the preparation and properties of ozone; and investigated plant constitution and physiological phenomena. He discovered and identified palmitic acid in palm oil, and synthesized the so-called Frémy's salt, a long-lived free radical used as a standard in electron paramagnetic resonance spectroscopy.

LIFE AND CAREER [1,2]

Edmond Frémy was born at Versailles on February. 28, 1814, the son of Victoire Julienne Tessier and François Frémy, a professor of Chemistry at the Saint-Cyr Military School, who gave to him his primary scientific instruction. In 1831, he began his formal chemical studies in Chemistry at Joseph-Louis Gay-Lussac's (1778-1850) laboratory *in l'École Polytechnique*, at the time when Théophile-Jules Pelouze (1807-1867) was the head of services. Frémy's academic career was very fast: in 1834, after finishing his studies, Frémy became *préparateur* in Gay-Lussac's courses; in 1837 he entered the *Collège de France* where between 1837-1846 he was *préparateur* of Pelouze, Thenard, and François Magendie (1783-1855); he was also *préparateur* and *répétiteur* of Pelouze at the *École Polytechnique* (1832-1846), and in 1846, succeeded him as professor (1846-1884). After the death of Gay-Lussac in 1850, Frémy replaced him at the chemistry chair in the *Muséum National d'Historie Naturelle* (1850-1892). In 1857, he was elected member of *the Académie des Sciences* replacing Louis-Jacques Thenard (1777-1857) who had just passed away; in 1875, he became president of the institution. In 1879, he was elected Director of the *Muséum* (1879-1892), replacing Michel Eugène Chevreul (1786-1889), who had just retired. Frémy was also director of studies in the second section of the *École Pratique des Hautes Etudes* and gave some courses at *the Écoles Centrale et du Commerce* (1834). In 1844 he was appointed member of the *Légion d'Honneur [chevalier* (1844), *officier* (1862), and *commandeur* (1878)]. Other honors included Commandeur de la Rose du Brésil*, Commandeur du Lion et du Soleil de Perse*, and *Chevalier de la Couronne de Fer d'Autriche*. He also served as Administrator of the Saint-Gobain glass factory.

Frémy married Mari de Louise Félicité Germaine Boutron one of the daughters of Antoine François Boutron Charlard (1796-1879). Frémy passed away on February 3, 1894, in Paris.

Frémy carried many research projects in inorganic and organic chemistry. His first researches were a continuation of those done by Pelouze on metal oxides; within them, he prepared ferric acid and ferrates, osmic acid, stannic and metastannic acids, antimonic and metantimonic acids, plumbic acid, zincates, bismuthates, cuprates, etc. His results indicated that oxides, considered indifferent or basic, became acid when reacting their hydrates with strong bases.[3] He prepared a large number of salts composed of oxygen, nitrogen, hydrogen and sulfur (sulfazotés), others based on cobalt, manganese dioxide, or containing two different acids.[4-8] One of the most famous of these is Frémy's salt, a long-lived free radical used as a standard in electron paramagnetic resonance spectroscopy. The original Frémy salt is disodium nitrosodisulfonate, $Na_2NO(SO_3)_2$. A variation of this salt, potassium disulfonate peroxylamine, $K_2NO(SO_3)_2$, is used nowadays as a source of long-lived free radical in the aqueous phase. It is also used as a standard in certain measurements in electron paramagnetic resonance spectroscopy.

Frémy tried unsuccessfully to isolate fluorine by electrolysis of melted fluorides; this led him to prepare for the first time a large number of fluorine salts and very pure hydrogen fluoride.[9,10] Together with Alexandre-Edmond Becquerel (1820-1891) they studied the preparation and properties of ozone.[11]

His work at the *Muséum National d'Historie Naturelle* led him to investigate the nature of the green matter of plants,[12-14] the composition of cerebral matter and bones,[15-17] the processes of fermentation, where he was an opponent of Pasteur's views,[18-20] the composition of pollen,[21] the coloring matter of flowers,[22] the ripening of fruits,[23] the composition of vegetable cells, and of different elements of plants and trees,[24-26] etc. etc.

Following the example of his teachers, Gay-Lussac, Pelouze, and Thenard, Frémy worked on many projects of industrial importance: for example, sulfonation, sulfation, and saponification of vegetable oils,[27,28] the separation (and discovery) of palmitic acid in palm oil and its further use in the manufacture of candles,[29] the manufacture of aventurine (a colored glass),[30] the synthesis of ruby,[31] the setting of hydraulic cement, the fabrication of cast iron and steel,[32] sulfuric acid, sugar beet, etc. etc.

SCIENTIFIC CONTRIBUTION

Frémy was a very prolific writer; he published over 100 papers and books in a variety of subjects.[20,33-38] Together ith Pelouze, his mentor, Frémy wrote several popular chemistry textbooks, and with the help of former students of the *École Polytechnique*, professors, and industrialists, published the *Encyclopédie Chimique*, a work in 10 volumes, where he was engaged for thirteen years until completing it 1894.

As customary of all candidates to a position in the *Académie des Sciences*, he published two brochures describing his scientific work and results,[39,40]

Here it is described a few of his results.

Esculic acid

The first scientific publication of Frémy was related to the acrid component present in the nut of the fruit of the horse chestnut (*Esculus hippocastanum*),[41] a work carried under the supervision of Pelouze. Frémy extracted the nuts with cold alcohol and evaporated the extract until a yellow gelatinous mass. This residue was completely soluble in water and alcohol, although its solubility decreased with a more concentrated alcohol. Treated with nitric acid, it decomposed and transformed into a yellow resin. The aqueous solution strongly foamed when agitated. According to Frémy, this substance had a very striking resemblance to the substance extracted by Antoine Bussy (1794-1882) from the saponin of the Egyptian saponaria. Frémy found that in addition to saponin, the horse chestnut contained a fatty material, easily extractable with ether, a yellow coloring matter, and a very bitter substance soluble in water and crystallizing in beautiful flakes.

Treating the saponin with an acid, HCl for example, the solution slowly became turbid and deposited a white acid substance, which Frémy named *esculic acid*. This deposition was faster when using hot HCl. The precipitate was insoluble in water and very soluble in alcohol, where crystallized back as small crystalline grains.[41]

According to Frémy, it was possible to separate highly pure esculic acid by first treating the horse chestnuts with cold KOH; this produced a combination with potassium of the yellow coloring matter and the esculic acid. Taking advantage of the fact that the coloring matter was insoluble in diluted alcohol while potassium esculate was highly soluble, he could easily separate the components. The potassium salt was then crystallized from the filtered alcohol solution and decomposed by addition of an acid.

Esculic acid was found to be insipid, slightly soluble in boiling water, very soluble n alcohol and insoluble in ether. Treated with nitric acid, it released nitrous gas and transformed into a yellow resin. Elementary analysis of the acid indicated that it contained 57.260 % carbon, 8.352 % hydrogen, and 34.388 % oxygen by weight, corresponding to the empirical formula $C_{52}H_{92}O_{24}$. Frémy found that only the esculate of potassium, sodium, and ammonia was soluble in water; these salts did not crystallize from their aqueous solution but did it when dissolved in a solution of 1 part of water and 2 of alcohol. The salts of barium, strontium, calcium copper and lead were insoluble,[41]

Frémy studied the behavior of the Egyptian saponaria under the same conditions and found that it also seemed to contain esculic acid; this acid had the same chemical and physical properties, and the same empirical composition as the one from horse chestnuts.[41]

Vegetable oils

Sulfation and sulfonation

According to Frémy, it was well known that sulfuric acid "saponified" oils yielding what were called sulfuric soaps. Chevreul had described the different products resulting of this reaction: fatty acids, a combination of sulfuric acid (sulfoadipic acid), and probably glycerin.[42] Frémy decided to study the reaction of vegetable oils with sulfuric acid; since almost all these oils yielded the same products, he concentrated his efforts on olive and almond oils. It was known, the reaction of vegetable oils with a base produced margaric (palmitic, [1]), oleic, and stearic acids as well as glycerin, so that it was possible to assume that olive oil was the composed of glycerin oleate and margarate. Treating olive oil with half its weight of concentrated sulfuric acid, the margarate first decomposed into margaric acid and glycerin and these combined with sulfuric acid, to form sulformargaric and sulfoglyceric acids. The oleate seemed to combine integrally with sulfuric acid, to form a double acid of olein and sulfuric acid (sulfoleic acid).[27]

Frémy found that sulfomargaric and sulfoleic acid were soluble in water, but in the presence of an excess of sulfuric acid, they became insoluble, forming a supernatant layer above an aqueous solution of sulfuric and sulfoglyceric acids. Treating the lower layer with calcium carbonate yielded immediately calcium sulfoglycerate. Sulfomargaric and sulfoleic acids were soluble in water and alcohol but the solutions did not crystallize. The aqueous solution had a bitter taste; at room temperature it decomposed very slowly and instantly at 100 ^{0}C. These acids formed water-soluble salts only with KOH, NaOH and ammonia. According to Frémy, the decomposition of sulfomargaric acid gave place to the formation of three solid fatty acids: (1) metamargaric acid, the salts of which had the same composition of margaric acid; (2) hydromargaritic acid, having the composition of margaric acid combined with two molecules of water; and (3) hydromargaric, corresponding to margaric acid combined with one molecule of water. Similarly, the decomposition of sulfoleic acid generated two liquid acids: metaoleic acid and hydroleic acid.[27]

Metamargaric acid was a white solid, melting at 50 ^{0}C, insoluble in water and soluble in alcohol and ether. Elementary analysis indicated that it contained (hydrated) 74.906 % carbon, 12.650 % hydrogen, and 12.444 % oxygen, corresponding to the empirical formula $C_{35}H_{69}O_4$. Meta oleic acid was a yellow liquid, insoluble in water, slightly soluble in alcohol, and very soluble in ether, having the composition (hydrated) 75.8 % carbon, 11.9 % hydrogen, and 12.3 % oxygen, corresponding to the formula $C_{35}H_{62}O_{3.5}$. The hydromargaric and hydroleic acids could be easily separated by taking advantage of their different solubility in alcohol: very low for the first acid and very high for the second one. Hydromargaritic acid was very white solid, crystallizing as rhomboidal prisms, melting at 68 ^{0}C, insoluble in water and soluble in alcohol and ether, and having the composition (hydrated) 71.86 % carbon, 12.22 % hydrogen, and 15.92 % oxygen. Hydromargaric acid was also a white solid, melting at 60 ^{0}C, insoluble in water and soluble in alcohol and ether and having the composition 73.82 % carbon, 12.46 % hydrogen, and 13.72 % oxygen. Hydroleic acid was a slightly colored liquid, insoluble in water, very soluble in alcohol and ether, and having the composition (hydrated) 73.9 % carbon, 11.8 % hydrogen, and 14.3 % oxygen.[27]

Heating hydro-oleic acid transformed it into water, CO_2 and two hydrogenized carbonated liquids, which Frémy named *oléène* and *elaène;* they contained hydrogen and carbon in the same proportions as olefiant gas (ethylene) but in a greater state of condensation. Oléène was a white liquid, boiling at 55 ^{0}C, lighter than water, highly inflammable, sparingly soluble in water, very soluble in alcohol and ether, composed of 85.74 % carbon and 14.72 % hydrogen, corresponding to the formula $C_{12}H_{24}$. Elaène was a white liquid, boiling at 110 ^{0}C, lighter than water, insoluble in water, soluble in alcohol and ether, composed of 85.42 % carbon and 14.63 % hydrogen, corresponding to the formula $C_{18}H_{36}$. Both compounds combined with chlorine forming a liquid chloride.[27] Frémy summarized the results of the sulfuric saponification as follows (a) all fatty materials treated with sulfuric acid transformed into a sulfo-fat acid and sulfoglyceric acid; (b) these double acids were decomposed by water into glycerin and fatty acids; and (c) the fatty acids produced were sometimes the same as those obtained during the alkaline saponification.[39]

In a following work, Frémy described the discovery of a new fatty acid present in palm oil.[29] He was led into the subject by the curious fact reported by Pelouze and Félix Henri Boudet (1806-1878) that a solid fatty acid separated from palm oil when saponified and also spontaneously.[43] Frémy separated the solid fatty acid from the oil, purified it

[1] Palmitic acid, C16H32O2, was discovered in 1813 by Chevreul and named margaric acid because it formed beautiful pearly crystals. Today, the name margaric acid is assigned to heptadecanoic acid, C17H34O2. Wilhelm Heintz (1817-1880) showed that Chevreul's margaric acid was probably a mixture of 10% stearic acid and 90% palmitic acid. This mixture possessed the melting point, crystalline form, and properties of margaric acid. In 1857 Heintz synthesized genuine margaric acid (C17H34O2).

by ordinary procedures, and found that it had a strong analogy with margaric acid (palmitic acid). The acid melted at 60 ^{0}C and contained 75.4 % carbon, 12.5 % hydrogen, and 12.1 % oxygen (the correct composition is 74.94 % carbon, 12.58 hydrogen, and 12.48 % oxygen). If heated to 250 ^{0}C and dissolved in alcohol, crystallized in small hard crystals, while before it did it in beautiful plates. Both crystal forms were found to have the same composition. Reaction of the acid with chlorine indicated that each equivalent of chlorine replaced the equivalent amount of hydrogen; the first chlorides were liquid at room temperature, the last ones were hard and transparent, as a resin. Frémy prepared a large number of palmitates and determine their composition. He named the new acid *acide palmitique* (palmitic acid).[39]

In 1855 Frémy was granted a patent for a saponification process of vegetable oils, based on the use of diluted sulfuric acid. The use of diluted acid did not result in the formation double acids (soluble in water) and release of SO_2 gas; in addition, the resulting fatty acids were not colored and thus could be used for the fabrication of candles.[28]

Composition of human brain

In a paper published in 1834, Jean Pierre Couerbe (1805-1867) gave an historical review of what was known about the composition of the brain and the results of the experiments he had carried, in order to isolate the immediate principles contained in the organ.[44] Many chemists had studied the composition of the brain: Louis Nicolas Vauquelin (1763-1829) had separated from it a red fat soluble in alcohol, a white fat soluble in boiling alcohol and precipitating on cooling as crystals, osmazone, lactic acid, and salts; Leopold Gmelin (1788-1853) and Kühn had added to these results the presence of a third another fatty material the brain. According to Couerbe, the available information was far from being clear. His experiments indicated that the brain, when examined with a powerful microscope, appeared to be composed of slightly elliptical globules, larger in the grey substance than in the white one, coagulable by acids, like those of milk and blood and by a great number of other substances. In particular, he found that the brain contained (a) a pulverulent yellow fat, *stéaroconote*; (b) an elastic yellow fat, *céranciphalote*; (c) a reddish yellow oil, *éléancephol,* (d) the white fat of Vauquelin, *cerebrate*, and (e) cholesterin (today, cholesterol), *cholesterote.* Added to these were the salts found by Vauquelin, lactic acid, sulfur, and phosphorus. Which formed a part of the fats listed above.

In a memoir read to the Académie des Sciences in 1840, Frémy wrote that he did not consider the substances separated from the brain by Couerbe to be first principles.[15,16] Couerbe had used only ether and alcohol to carry on the separation and purification of the components of the brain; Frémy believed that the properties of the brain components were so similar that it was difficult to accept that these solvents were able to separate them completely. His first results indicated that the human brain contained 80 parts of water, 15 of albumin, and 5 of fatty material. Since a chemical analysis of the albuminous portion showed the usual properties (insoluble in water, alcohol, and ether), Frémy devoted all his efforts to the analysis of the fatty matter, which could be extracted with ether and alcohol. The brain was first cut into small pieces and then extracted several times with boiling alcohol in order to coagulate the albumin and eliminate most of the water, which prevented ether to act properly. The cerebral mass lost its elasticity and could be pressure squeezed; the alcohol retained only traces of cerebric acid, which could be separated by filtration; on cooling, the alcoholic extract deposited a white substance, which contained phosphorus and was the same as that one discovered by Vauquelin. The extract did not hold fatty materials and was frankly acid because of the phosphoric acid it contained.

The solid material left after treatment with alcohol was then extracted several times with boiling ether and the mixture of these extracts was concentrated by distillation until it became viscous. The dry residue was fractionated by a series of extractions with boiling alcohol, cold ether, slightly acidulated alcohol, aqueous ammonia, etc. Frémy found that the portion soluble in ether was formed chiefly of these substances: (a) The white matter discovered by Vauquelin, having clear acid properties and which Frémy called *cerebric acid*; (b) cholesterin, (c) a particular fatty acid, which he named oleophosphoric acid and (d) traces of oleic, margaric and other fatty acids. Frémy remarked that these immediate principles were never present as isolated compounds, for example, cerebric acid was always combined with sodium or calcium phosphate, and oleophosphoric acid was always present as sodium salt.

According to Frémy, neglecting the fatty materials, typical of animal matter, the results of the analysis indicated that the brain was characterized by the presence of cholesterin and two particular fatty acids; a composition much more simple than the one claimed by Couerbe.[15,16]

In the following section of his memoir, Frémy reported the analysis of cerebric acid, oleophosphoric acid, olein, cholesterol and the fatty acids present in the brain. Cerebric acid was a crystalline substance completely soluble in boiling alcohol, almost insoluble in cold ether and more soluble in boiling ether. It had the particular property of swelling in boiling water like starch, while remaining insoluble. It melted at a temperature very close to that of its decomposition. Burned with potassium nitrate and carbonate did not produce potassium sulfate, but a certain amount of phosphate. An elemental analysis indicated that it contained 66.7 % carbon, 10.6 % hydrogen, 2.3 % nitrogen, 0.9 % phosphorus, and 19.5 % oxygen, by weight. Frémy reported that he was unable to prepare pure oleophosphoric acid; his product always contained cholesterol and cerebric acid. The acid was normally a yellow viscous substance, insoluble in water and in cold alcohol; it was soluble in boiling alcohol and in ether. In contact with KOH, NaOH and ammonia it generated immediately soapy combinations. Boiled for a long time in water or in alcohol, it lost its viscosity and became a fluid oil, which should be considered pure olein. The liquor was strongly acid due to the phosphoric acid it contained. Nevertheless, its reactions indicated that oleophosphoric acid should not be considered a mixture of olein and phosphoric acid; it was probably a combination of these compounds.[15,16]

Frémy examined the purified olein fraction and described it as a greasy yellow fluid containing 79.5 % carbon, 11.9 % hydrogen, and 8.6 % oxygen, by weight (the actual composition is 77.32 % carbon, 11.84 % hydrogen, 10.84 % oxygen). Olein saponified easily with alkalis, yielding oleate and glycerin.

Frémy summarized his results by saying that the human brain contained cerebric acid free or combined with sodium or calcium phosphate; (b) oleophosphoric acid, free or combined with sodium; (c) olein and margarine [1]; (d) small amounts of oleic and margaric acids; (e) cholesterol; and (f) water and albuminous matter.

Frémy also prepared and analyzed the different components reported by Couerbe. He concluded that cérébrote was actually a mixture of cerebric acid, calcium cerebrate, and cerebral albumin. Similarly, céphalote was not a pure substance but a mixture of calcium or sodium cerebrate with traces of albumin and oleophosphoric acid; stéaroconote was mixture of cerebral albumin with traces of the sodium or calcium cerebrates and oleophosphates, and finally, éléencéphol was a mixture of olein, oleophosphoric acid, cerebric acid, and cholesterol.[15,16]

In analyzing the brain in different states and of different ages, Frémy found that the quantity of free fatty acids was variable; and even sometimes increased when the fatty matter was left in a closed bottle. He explained this curious phenomenon by referring to the observations of Chevreul on the fat of cadavers[45] and to the memoir of Pelouze and Boudet[43] describing the spontaneous saponification of palm oil. He further observed that the albuminous matter of the brain, had the property of eventually converting the olein into oleic acid. Lastly, he found that all the fatty bodies occurred in the white substance of the brain and that the gray portion contained only traces of it; therefore if the anatomy of the brain were analyzed from a chemical point of view, it could be said that the substance forming the frame of the brain was originally gray, and that the fatty matter was which infiltrated and spread into of the gray matter and formed the white zones, which constitute the white portion of the brain.[15]

Fluorides and fluorine

In 1836, Alexandre-Edouard Baudrimont (1806-1880) communicated to the Académie des Sciences that he had succeeded in isolating fluorine. According to Baudrimont, he had done it by passing a stream of boron fluoride over minium (Pb_3O_4), heated red and collecting the gas released in a dry vase; or by treating in an hot ampoule a mixture of calcium fluoride and manganese dioxide, with sulfuric acid. In the first procedure, the gas had a yellow-brown color and smelled like chlorine or burnt sugar; it did not attack glass, it bleached indigo and combined directly with gold. In the second procedure, the fluorine was mixed with hydrogen fluoride (HF) and fluosilicic acid, which did not allow observing its main properties.[46] In 1841, Paulin Louyet (1818-1850) reported that he had repeated Baudrimont's experiments and concluded that the gas obtained by the second procedure did not contain fluorine gas; it was actually a mixture of chlorine, hydrogen fluoride, fluosilicic acid, and oxygen. All these originated from the impurities present in the calcium fluoride employed by Baudrimont. Louyet repeated the experiment this time using a white opaque calcium fluoride and once again, he found that the gas generated was simply impure chlorine. The gas dissolved in water and communicated to it its color and odor; it bleached tournesol and indigo, and produced a white precipitate with silver nitrate. The latter result was a strong proof that the gas was not fluorine because silver fluoride was very soluble in water. In addition, a solution of the supposed fluorine exposed to sunlight, lost its color and odor, became acid, but did not corrode, showing that it could not be (HF). A third experiment was carried on using crystalline spathfluor deprived of silica. In this situation, Louyet obtained a mixture of HF and fluosilicic acid, as proved by the strong corrosion of the glass. Louyet also found that reacting an aqueous solution of HF with manganese dioxide produced manganese fluoride and not free fluorine [2].[47]

In a following paper Louyet described the series of experiments he had carried on to determine the equivalent of fluorine. Initially, he carried on the calculation by determining the quantity of calcium sulfate yielded by a certain weight of the purest natural calcium fluoride and also of a fluoride, prepared by synthetic means. Although the two series of experiments agreed very well, he was not completely certain of their accuracy because he had found that the same experience carried on with lead fluoride, proved that sulfuric acid did not completely decomposed lead fluoride, and perhaps the same phenomenon took place with calcium fluoride and the synthetic fluoride. For these and other reasons, Louyet repeated the experiments with calcium fluoride, taking special care to carry them as exact as possible. The new set of six experiments indicated tha the average weight of calcium sulfate obtained from one gram of

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[1] Ver página 155.

[2] Paulin Louyet died in 1880 of poisoning caused by breathing HF gas.

calcium fluoride was 1.7436, corresponding to a value of 237.50 for the equivalent of fluorine and 19 for the atomic mass (the correct value of 18.9984).[48] Interestingly enough, Louyet used his results to reject Ampère's hypothesis that fluorine should be consider an analog of chlorine, bromine, and iodine.[49] He believed that fluorine formed a class by itself and, if necessary to link it to some simple bodies, it should be to oxygen, sulfur, nitrogen, phosphorus, etc., that is, to the series of simple bodies whose equivalents were whole multiples of the equivalent of hydrogen (Prout's hypothesis).

As reported by Frémy, he had witnessed some of Louyet's experiments and found then unsatisfactory; for this reason he decided to carry on his own tests.[9.10] The first part of the two memoirs he published on the subject of fluorides was devoted to the preparation of pure anhydrous hydrogen fluoride. He did it by distilling hydrofluate of potassium fluoride (potassium hydrogen difluoride, KHF_2) in a platinum distillation still. The starting salt was prepared by adding HF (impure) to potassium fluoride; the very low solubility of fluorhydrate fluoride led to his immediate precipitation. The precipitate was purified by successive crystallizations, followed by drying. The anhydrous HF obtained by distillation, was gaseous at room temperature, but could be condensed by a mixture of ice and salt into a very fluid liquid volatilizing when removed from the refrigerating mixture, acting very powerful on water and diffusing white fumes in the air. Contrary to Louyet's assertion, anhydrous hydrofluoric acid attacked glass rapidly.[9.10\]

Frémy used the HF thus prepared to synthesize the fluorides of K, Na, Ca, Pb, Sn, Hg, Ag, Zn, etc. He also studied the action of several reagents upon calcium fluoride: hydrogen, water vapor, oxygen, chlorine and carbon disulfide. From the many experiences carried on he reached the following conclusions: (a) HF could be obtained anhydrous and pure, by calcining in an apparatus of platinum hydrofluate of fluoride of potassium, previously well dried. In this state, the acid was gaseous at ordinary temperatures and attacked glass and all siliceous substances energetically, contrary to what has been asserted on the subject in last few years; (b) All the experiments made confirmed this acid was an hydroacid (did not contain oxygen); (c) The fluorides could be divided into three classes, each one characterized by certain important properties. The first class contained the anhydrous fluorides, which were comparable to the chlorides; the second class, the hydrated fluorides, which behaved like the hydrochlorides; in the third class were found the hydrofluates of the fluorides, which were true acid salts; (d) The anhydrous fluorides were remarkable for their stability; the hydrated fluorides, on the contrary, were only slightly stable, and were decomposed even when dried under vacuum, HF was disengaged, and left a residue of oxyfluoride or oxide; (e) The anhydrous fluorides had a strong tendency to form double fluorides; this property was seen even with insoluble fluorides. These last compounds could be obtained by double decomposition, they always retained as a double salt, part of the soluble salt used in their preparation; (f) At high temperature, hydrogen did not decompose all the fluorides; nor act on fluoride of calcium, but it easily reduced the fluorides of lead, of tin, etc. The reduction by hydrogen of metallic fluorides such as those of lead and tin, etc., which resisted the reducing action of carbon, appeared to demonstrate in a positive manner that these compounds contained no oxygen, and were really binary compounds; (g) All the fluorides, even those of potassium, sodium, and calcium, are rapidly decomposed by water vapor; (g) Oxygen and chlorine decomposed calcium fluoride at furnace heat and liberated a gas, which appeared to be fluorine; (h) Sulfur vapor did not act on calcium fluoride, but this body was completely decomposed by carbon disulfide vapor, forming calcium sulfide and probably carbon fluoride; the presence of siliceous substances facilitated the reaction; (h) The analyses of the principal fluorides made in this work such as those of potassium, sodium, calcium, tin, lead, and silver, showed that the equivalent of fluorine, as determined by Berzelius, was correct: (i) All the fusible fluorides were decomposed by the voltaic current, and disengaged a gas, which appeared to be the radical of fluorides.[9,10]

Frémy also reported that he had tried unsuccessfully to prepare fluorine. It was left to Henri Moissan (1852-1907), his student, to achieve this goal in 1886 and, as a result, receive the 1906 Nobel Prize in Chemistry. Moissan obtained fluorine by electrolysis of a solution of potassium hydrogen difluoride. Frémy had tried unsuccessfully to prepare the element by electrolysis of molten fluorides.[50]

Ozone

It was known that heat was able to introduce remarkable modifications in the properties of certain substances such as sulfur and phosphorus. Frémy and Becquerel were intent on finding if electricity was also able to change the properties of bodies, particularly oxygen.[11] In the first part of the memoir they published on the subject, they made an historical review of all the experiences that had been done about ozone. Martinus van Marum's (1750-1837) was probably the first to report that ozone had a particular odor. At the end of the 18th century he had used the large electrical machine in Teylers Museum (Haarlem, Netherlands) to study the effect of strong sparks on different substances, particularly gases. He reported that after passing 5000 sparks through a glass tube filled with oxygen, the gas showed no reaction on water, limewater, or tournesol, but had acquired a very strong and characteristic odor, which he believed *was clearly the smell of the electrical matter*. When using purer oxygen and a thinner glass tube, Van Marum noticed some additional effects: the mercury had became strongly oxidized at his surface and the tube was covered with the oxide of the metal. He remarked, "it was evident that in this experience the principle of pure air (oxygen) has united with the mercury". Van Marum's experiments had proved that the electrification of oxygen resulted in the formation of a characteristic odor and had given the gas the ability of rapidly combining with oxygen, an effect that took place very slowly at room temperature.[11]

According to Frémy and Becquerel, Van Marum's results were essentially forgotten until 1840 when Christian Friedrich Schönbein (1799-1868) described a particular odor that accompanied the oxygen produced during the decomposition of water by a voltaic pile, and gave a detailed account of the properties of the gas. Schönbein named the odorant substance *ozone* and reported that it had the following properties: (a) it was destroyed when passing through a tube heated to 250 ^{0}C, and also at room temperature when in contact with carbon; (b) it had the same odor as chlorine; (c) it was insoluble in water, promptly destroyed coloring organic substances, as well as ligneous and albuminous matter; (d) ozonized atmospheric acid in contact with limewater, generated appreciable amounts of calcium nitrate. Ozone changed SO_2 into SO_3; (e) it reacted energetically with metals and oxidized them to their highest degree; and (f) it decomposed KI generating iodine. Hence the most sensitive reagent for detecting the presence of ozone was a strip of starched paper containing a small amount of KI (this test became known as an ozonoscope). Originally Schönbein believed that ozone was a nitrogen compound; afterwards that it was a hydrogen peroxide, and eventually, that is was a modification of oxygen.[51]

Alexander Williamson (1824-1904), Justus von Liebig (1803-1883), François Arago (1785-1853), Jean Charles de Marignac (1817-1894), and Auguste-Arthur de la Rive (1801-1873), published further results. Marignac and de la Rive demonstrated that ozone. Could be formed without the presence of nitrogen; it could be generated within pure dry oxygen; and electrifying CO_2, dry or humid, did not generate ozone, They concluded that ozone was not a simple body nor a combination of hydrogen and nitrogen; its effects were actually caused by oxygen in a particular state of chemical activity generated by.[52,53]

Frémy and Becquerel summarized their historical review saying that it was impossible to identify the nature of the ozone gas that resulted from the action of humid air on phosphorus, it could contain yet unknown oxygenated compounds of phosphorus, hydrogen, or nitrogen; the observed oxidation reaction that had been observed could well be attributed to these different substances. The oxygen released during the decomposition of water in a cell, which presented all the characteristics of ozone, could well be mixed with small quantities of oxidizing materials, generated under the influence of electricity by the action of nascent oxygen on the air dissolved in the water, or on the acid added to the liquid, or even, by the elements of water itself. The oxygen released by melting potassium chlorate, and ozonized by the electrical sparks, perhaps contained traces of potassium chloride or of an unknown chlorine compound, which, under the action of electricity, released enough chlorine to slightly blue a strip of paper containing starch and KI. Finally, the reactions observed every time that an electrical spark traversed atmospheric air, could maybe be attributed to the influence of an oxygenated compound of nitrogen, formed at the time of passage of the spark.[11]

In a lengthy series of experiments, Frémy and Becquerel repeated all the experiments that previous researchers had performed to provide oxygen with the special properties of ozone. The ozone was prepared by electrical or chemical means. The electrical means included the Ruhmkorff coil, circuit breakers, a voltaic cell, electricity by influence (see below), etc. The chemical means included calcination of the oxides of manganese, mercury and silver, and decomposition of potassium chlorate. In every possible case, the presence and amount of ozone produced were detected using an ozonoscope. Whenever appropriate, Frémy and Becquerel determined the action of sparks on oxygen prepared from different sources, the influence of humidity (dry and wet oxygen); the action of electrified oxygen on pure water, on a solution of KI or AgI and on wet silver or wet mercury. Their lengthy memoir gives a detailed description of the experimental apparatus and procedure used for every alternative.[11]

Their conclusions were as follows: (1) they had verified all the results reported by Schönbein and Marignac, related to the oxidation properties of oxygen produced by the decomposition of water in a voltaic cell. This method could not be employed to determine the nature of ozone because this compound was present in a very weak concentration; (2) the electrical arc produced by a circuit breaker did not seem to modify oxygen in the same manner as an ordinary spark, probably because the accompanying increase in temperature destroyed what was produced by electricity. Nevertheless, this means could be used to determine the combinations of different gases, by acting as platinum sponge and electricity. In this manner, Frémy and Becquerel had combined nitrogen and oxygen to form NO_2, hydrogen and nitrogen to form ammonia, and SO_2 and oxygen to form SO_3; (3) the spark produced by the Ruhmkorff coil, acted like the spark produced by other electrical means, and permitted an easy duplication of any given experiment; (4) it was possible to electrify pure oxygen enclosed in a glass tube (containing an ozonoscope) by means of a series of sparks licking the external surface of the tube, as shown by the blue color generated in the ozonoscope (electricity by influence). It was remarkable that oxygen could be electrified without the intervention of metal wire, and consequently, in the absence of the particles transported by sparks; (5) oxygen prepared by the most different ways (e.g. chemical means, a voltaic cell, etc.) acquired the characteristic smell of that one subjected to the influence of electricity. This oxygen lost its oxidizing properties when contacted with KI and recovered its odor and chemical properties when electrified again. All these results proved that the oxidizing power of electrified oxygen was not due to the presence of a foreign substance in the gas; and (6) electrification of pure and dry oxygen in a glass tube during a long time (many hours) showed that the modification increased, first proportionally to the time of electrification and then seemed to decrease, because the sparks destroyed what they have previously produced. Lastly, Frémy and Becquerel repeated their statement that all their experiments had been carried out in closed tubes containing pure oxygen and wet potassium or silver iodides, just to prove that nitrogen was not part of the particular activity awarded by the electrical sparking to oxygen.[11]

For all the above reasons, Frémy and Becquerel believed that the proper name for the gas activated by electricity should be *oxygène électrisé* (electrified oxygen) and not ozone, which expressed the transformation of oxygen into another body.

Chlorophyll

According to Frémy, a number of researchers considered the green matter of leaves to be an immediate principle, which they named chlorophyll, while others thought it was a mixture of different substances.[12] Some believed it contained nitrogen, others that it was constituted of three different elements, while François Verdeil (1747-1832) had announced that chlorophyll was related to the coloring matter of blood, and as so, it contained iron.[54] Frémy believed that the conflicting evidence simply proved that chlorophyll had never been obtained in a sufficiently pure state to determine its real composition. It was known that that alcohol dissolved easily the coloring matter of leaves and that evaporation of the extract left the green oil called chlorophyll. Frémy prepared this extract and then treated it with alumina hydrate, a well-known adsorbent of coloring matters. The affinity of this adsorbent could be increased or decreased by adding water or absolute alcohol. In his particular application, Frémy observed that a highly alcoholic extractant produced a yellow extract and left a deep green gum-lac; when using a very dilute extractant all the coloring matter united with alumina and generated a yellow green gum-lac that reminded exactly the coloration of leaves. From these results, Frémy assumed that chlorophyll was constituted of two coloring matters, a blue and a yellow one, which he named phyllocyanin and phylloxanthin, respectively. After trying a large number of substances for separating them (e.g., ether, carbon disulfide, turpentine, etc.) Frémy selected a mixture of ether and HCl. He placed into a stoppered bottle, two parts of ether and one part of hydrochloric acid, diluted with a little water, shook the bottle strongly for some time, and then added the green oil extract. The effect was very remarkable: The ether dissolved the yellow matter of the leaves and became of a beautiful yellow color, while the hydrochloric acid reacted upon the green matter, which had been bleached and produced a magnificent blue. As a result, the two colors had been separated and retained by two different solvents; mixing the two liquid phases did not regenerate the original green color. This result was easily obtained by adding alcohol, which produced a homogeneous system, colored green as chlorophyll.[12]

In the following stage, Frémy decided to compare the green matter of leaves with the yellow substance found in young shoots and, mainly, in wilted leaves. His results indicated that in these two circumstances, the yellow substance of the leaves was present in the same state as the one that resulted from the decomposition of chlorophyll: It was easily extracted with alcohol and transformed into the blue matter under the double influence of ether and HCl. Wilted leaves, under the influence of HCl vapors acquired rapidly a beautiful green coloration. The yellow autumn leaves did not contain phyllocyanin; they were colored only by phylloxanthin. This proved that phylloxanthin was more stable than the blue matter; it was still present in fallen leaves, suggesting that phylloxanthin was a result of the plant physiology.[12]

Frémy also found that under certain circumstances, phyllocyanin was capable of yielding another yellow substance, which he named phylloxanthein; from this substance phyllocyanin may be again obtained.[12]

In a following publication, Frémy wrote that in spite of all his efforts, he had been unable to make a detailed study of phylloxanthin and phyllocyanin because of the great difficulties he had encountered trying to separate them. Phylloxanthin, soluble in ether, was always extracted together with some fatty components, which he could not eliminate. Also, he was not sure that the strong acid that held phyllocyanin in solution did not affect it. Weaker acids unfolded chlorophyll into a mixture of its two main components, without facilitating their separation. For these reasons, he went on to study the effect of different bases. His results indicated that these reagents seemed to act on chlorophyll in three different ways: (a) Certain hydrated alkaline earths, such a alumina and magnesia, combined with the green substance forming true gum-lac; (b) alkaline bases such as KOH and NaOH, boiled in the presence of chlorophyll, unfolded it like acids, but at the same time, they saponified the accompanying fatty materials, producing a green soapy liquid; (c) with other alkaline earths such as chalk and barite, the reaction was more distinct. Boiling an alcoholic solution of chlorophyll with baryte hydrate split it and the phylloxanthin, which is a neutral body insoluble in water, precipitated together with a barium salt of phyllocyanic acid. Thus chlorophyll was seen to be a sort of colored fat, which was saponified by strong bases, where the phylloxanthin appeared to be glycerin and the bluish-green phyllocyanic acid the fatty acid.[13]

Frémy found that alcohol dissolved the phylloxanthin from the mixed precipitate; evaporation of the alcoholic extract resulted in the precipitation of crystals, sometimes as yellow plates and sometimes as reddish prisms. These crystals were insoluble in water, but soluble in alcohol and ether, and possessed considerable tinctorial power. The barium salt of phyllocyanic acid was then decomposed by sulfuric acid; the phyllocyanic acid was found to be soluble in alcohol and ether.[13]

In spite of all these results, Frémy did not think that chlorophyll was not a simple mixture of a yellow and blue body. He believed that chlorophyll was an immediate green principle of excessive changeability, which, under the influence of reagents, and probably by the action of vegetation, underwent various modifications, and produced the two colored bodies he had discovered.[13]

In a third publication, Frémy reported that he had found, not only that the alcoholic extract of chlorophyll contained substantial amounts of potassium, but also that this amount was proportional to the intensity of coloration of the liquid. Evaporation of the extract, followed by calcinations, proved that the solid residue contained very pure potassium carbonate. In order to test the possibility that the green matter of vegetables was due to potassium phyllocyanate, Frémy prepared this salt by treating an alcoholic solution of barium phyllocyanate with potassium sulfate; to his satisfaction, he noticed the precipitation of barium sulfate and the formation of a splendid green solution. The same results were obtained when replacing the potassium sulfate by sodium or ammonia sulfate. Frémy carried on a spectroscopic inspection of potassium phyllocyanate and observed that it gave the same black line of absorption, located in the middle of the red part of the spectrum, which Jules Chautard (1826-1901) had reported in his work about chlorophyll.[55] From these and other results, Frémy concluded that the coloring matter of leaves was a mixture of phylloxanthin and potassium phyllocyanate.[14]

Colored glass

According to Frémy and Louis Clémandot (1815-) (an engineer working at Clichy) although the manufacture of colored glasses had been recently introduced into France, it had progressed so fast that it competed successfully with the glasses imported from Bohemia.[30] Nevertheless, the French artisans had been unable to develop a process for manufacturing artificial aventurine (natural aventurine is a species of quartz that contains throughout its mass a number of brilliant spangles of mica). The Venetians had succeeded in producing a glassy compound, which rivaled the natural one; their aventurine was a yellow glass where were disseminated, a very large number of very small copper crystals resulting of the reduction of cuprous oxide by ferrous oxide. Ferric oxide gave the yellowish color to the glass while the copper crystals remained disseminated in the mass. The Venetian aventurine was manufactured in Murano using secret procedures and constituted a lucrative article of commerce, being sold in France at about 200 francs per kilogram.

Frémy and Clémandot decided to investigate the possibility of discovering the possibility of making this gem to benefit the French economy. For their purposes, they used the facilities of the Clichy glass factory, which had recently been installed at Clichy-la-Garenne. Their starting point were the chemical analyses of aventurines reported by Friedrich Wöhler (1800-1882) and Charles Barreswil (1817-1870); they had found that the Venetian aventurine was composed of a soft glass holding in suspension metallic and crystallized copper. This information suggested the possibility of preparing aventurine by crystallizing copper in melted glass, and keeping the mixture in such a state that the metallic crystals would remain disseminated through the vitreous mass. After much experimentation, Frémy and Clémandot found that under the action of heat, iron scales promptly reduced cuprous oxide to the metallic state, while passing itself to the state of iron peroxide. This reaction appeared well suited to answer the question because it produced pure copper and formed a metallic oxide, soluble in the glass, and giving it only a slight yellow tint. The parallel formation of a silicate of iron peroxide was a fortunate circumstance, so that, by increasing the density of the glass, this silicate would naturally oppose the deposition of the metallic crystals. The manufacturing procedure consisted on heating for twelve hours a mixture of 300 parts of powdered glass, 40 parts of cuprous oxide, and 80 parts of iron scales, and then allowing the mixture to cool very slowly. The result was a vitreous mass, somewhat opaque, containing abundant crystals of metallic copper; a microscopic examination showed that the copper was crystallized in regular octahedrons, the same as in Venetian aventurine.[30]

Some years later, Pelouze succeeded in preparing a variation of Venetian aventurine glass by adding potassium dichromate to the melt.[56] Potassium dichromate produced the sesquioxide of chrome, which, in enough quantity, gave to the glass a transparent green color and its crystals remained in suspension into the glass mass. Chrome aventurine, as named, 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.[57]

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