Revista CENIC Ciencias Químicas, Vol. 33, No. 3, 2002.

RESEÑA BIOGRAFICA

Louis-Jacques Thenard.

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Recibido: 17 de junio de 2002 Aceptado: 17 de diciembre de 2002

Palabras clave: Thenard, agua oxigenada, boro, potasio, sodio, catalisis.
Key words: Thenard, hydrogen peroxide, boron, potassium, sodium, catalysis.

RESUMEN: A Louis-Jacques Thenard (1777-1857) le debemos el descubrimiento del agua oxigenada, y del boro, la aislación del potasio y sodio por medios químicos (junto con Gay-Lussac), y la síntesis de muchos de sus compuestos, tales como la amida de potasio y el trifluoruro de boro. El también demostró la acción catalítica ejercida por la esponja de varios metales (osmio, rodio, paladio e iridio) sin entender la naturaleza de su actividad.

ABSTRACT: To Louis-Jacques Thenard (1777-1857) we owe the discovery of hydrogen peroxide and boron, the isolation of potassium and sodium by chemical means (together with Gay-Lussac), and the synthesis of many of their compounds, such as potassium amide and boron trifluoride. He also demonstrated the catalytic action exerted by the sponge of several metals (osmium, palladium, rhodium, and iridium) without understanding the nature of their activity.

There are two important eulogies written for Thenard, one by Pierre Flourens (1794-1867)[1] and the other by Frederic Dubois.[2] Although they are significantly different in their approach but coincide in the main scientific facts, it is interesting to note that Dubois accuses Flourens several times of inaccuracy in reporting certain facts. In a footnote that appears in the third page of his eulogy Dubois writes that "Je vais me recontrer ici pour la troisième foi avec M. Flourens" (I meet here Mr. Flourens for the third time). He then indicates that in his eulogy for Thenard, as well as on his memoirs about the work of Magendie and of Geoffroy Saint-Hillarie Flourens has taken an anecdotic approach instead of a scientific one and this has led him to report several facts inaccurately. Dubois bases his arguments on conversations he held Michel Eugéne Chevreul (1786-1889), who lived long enough to know all of the characters mentioned.

Part of the conflicting facts is given in the text that follows.

Life and career

Louis-Jacques Thenard (Figure 1) was born on May 4, 1777 in La Louptière, department of l'Aube. He was the second child of Etienne-Amable Thenard and Cécile Savourat, farmers and tenants in a large state that belonged to the Montessus family. His mother had, from a previous marriage, one daughter. Together with Amable they had four sons and two daughters. His oldest brother, Antoine, studied at the *École Polytechnique* and then at *Ponts et Chaussées*. Eventually he became chief engineer of Ponts et Chaussées. To his credit stands the invention of movable dams for rivers.

When Louis-Jacques was nine years old, knowing to read and write, he was put under the educational tuition of the Abbé Maget, priest of Ville-neuve-l'Archvéque. His progress was very rapid and two years later, the priest advised his father to send him to the *Collège de Sens*, The Revolution interrupted his studies but one of his teachers, Bardin, was so impressed by his abilities that instead of returning him to his home, he kept him and made him complete his literary studies.

In the meanwhile, Thenard's father, disgusted by the political events, had abandoned the rich family farm in la Loutiére, where the business, which had been very prosperous under the King, had become poor under the Terror, and, for the welfare of the family, retired to Courceaux. In addition, he was very worried how to stand the payments of a farm he had recently purchased in Le Courtillot. What to do with the young boy; bring him back to the family house and sacrifice all the years of education or send him to Paris, where he was not sure he could support him economically. His mother decided for the last course. Accompanied with two friends, Louis-Jacques landed in a house located across the *École de Médicine*, managed by Madame Bateau.

Once in Paris, the studies of Louis-Jacques turned to pharmacy. He took the courses given by Antoine-François Fourcroy (1750-1809) and Louis Nicolas Vauquelin (1763-1829); after many lessons he realized that he had taken the wrong direction, that in order to understand the laws and the facts he was learning, he had to learn how to use the instruments and the equipment that would give him a feeling of what he was learning. For this reason, at the age of seventeen, he approached Vauquelin and offered to serve him as laboratory assistant as payment of the lessons and food. According to Flourens[1] Vauquelin who was very poor, admitted to his service only students who could pay twenty francs per month. Vauquelin was about to refuse his request for lack of funds, when entered his two sisters (who at the time were divorced and kept house for him), who were so impressed by the young man that they recommended his brother to accept the request: "Mais il est gentil ce petit; tu devrais le garder, il aiderait dans le laboratoire et surveillerait le pot-au-feu, que tout tes muscadins laissent trop bouillir" (How kind is this little one, you should keep it, it would help in the laboratory keeping an eye on the beefbroth, left too much on the fire by all your dandies). Dubois rejects this story[2] saying this dialogue never took place, that Vauquelin had not sisters and that two ladies were actually Fourcroy's sisters. In addition, that Chevreul told him that neither Vauquelin nor Thenard were that poor that the first would have refused. the request and the second had to take kitchen chores.

Thenard served Vauquelin in this position for three years, without improving his economic position. In a certain opportunity Vauquelin received a sample of the emerald of Limoges to be analyzed; pressed by other tasks he assigned it to his senior student, who asked Thenard to help him. After many experiences the student reported to Vauquelin that the mineral contained only known elements. Thenard continued the work and after one month he reported to Vauquelin that the Limoge emerald contained a new substance. Vauquelin asked him to repeat all the experiences and after three days he was handed 250 grams of glucine.[3] Thenard was then 20 years old. Now Vauquelin took care of his career and had him appointed professor of chemistry in an institution directed by Lemoine for the children of well-to-do families.

In a certain opportunity the needs of the war required of Vauquelin to leave Paris and go to Rouen to help in the war effort; he requested from Thenard to take over the course he was teaching. Thenard did this with such a success that afterwards he was appointed *répétiteur* to Fourcroy, at the *École Polytechnique* with a salary of 1,500 francs, a fortune for him.[3] This appointment meant having a large laboratory at his disposal; now he could dedicate to work for himself. In April 1804, Thenard resigned to take up a chair at the Collège de France and Gay-Lussac was appointed in his place.

Thenard's first independent research was on the oxides of antimony and their reactions with hydrogen sulfide.[4] This publications was followed by other studies about phosphorus, nickel, alloys of nickel antimony and tin, the yellow and red sulfides of arsenic, nitric, oxidation processes in general and of iron in particular, cobalt oxides, ammonia, sodium and ammonium phosphates, tartrates, wine fermentation, artificial camphor, sebacic acid, coagulation of albumin by heat and acids, bile and biliary gallstones, and on diabetes sugar.

Jean-Antoine Chaptal (1756-1832), whom Napoleon had appointed Minister of the Interior, commissioned Thenard to find a replacement for ultramarine blue, an imported material which was basic for the production of porcelain at Sèvres. Within fifteen days, Thenard succeeded in synthesizing cobalt blue [Thenard's blue, blue cobalt aluminate, $Co(AlO_2)_2$] and a month afterwards this material was already being used to decorate the vases produced at Sèvres.[5]

A year later, in a soda industry near Marseille, an oven brick was discovered accidentally which in contact with the product of the process, yielded the true ultramarine blue. At that time Thenard was president of the *Societé d'Encouragement* and as such he proposed a prize of 14, 000 francs for a process for producing the product. Jean-Baptiste Guimet (1795-1871), a student of Thenard, succeeded in doing it, and with it Thenard's blue disappeared from the market. This achievement meant that after thirty years, during which Europe consumed only two kilograms per year, at a price of 10 000 francs per kilo, was now consuming 2.4 millions, at a price of fifty sous per kilo.

Another subject of discrepancy between Flourens and Dubois relates to the painting of the dome of the Pantheon at the church of Sainte-Geneviéve, which had been recently done by Antoine-Jean Gros (1771-1835) and had become a much visited and admired work of art. Eighteen months after it was finished, pieces of the ceiling started to detach and fall because of humidity problems, causing serious damage to the painting. According to Flourens[1] Thenard, who was a close friend of Gros, did some experimental work and found the way to make stones and cement waterproof. With this result he approached Gros and asked him if he would be willing to repair the dome if Thenard would guarantee that the problem would not return. Thenard was invited to the Tuileries Palace to be congratulated by Napoleon, receive his approval of the project, and the decision to start repairs the next day. Dubois[2] claims that Flourens was driven by his imagination and that the facts were quite different. He justifies his accusation by quoting by a paper written by Thenard and Darcet on the subject[6] where they report that *Gros approached them* before the painting to know if the dome structure was appropriate for the work. Thenard and Darcet advised Gros that humidity would eventually be a problem but that impregnating the stone with a fatty material would eliminate it.

Academic career

Louis Thenard served in many in academic positions: Répétiteur of chemistry at the École Polytechnique (1799); Professor at the Collège de France (1804), Professor of chemistry at the Faculté des Sciences de Paris (1809), Professor of chemistry at the École Imperiale Polytechnique (1811), member of the Societé d'Arcueil (1806), Dean of the Faculty of Sciences of Paris (1822), and Chancellor of the Université de France (1845-1852). The latter position corresponded to the highest French academic post.

Honors and appointments

Thenard received many honours and appointments for his contribution to science and industry. He was member of the Comité Consultatif des Arts et Manufactures (1813), Conseil de Perfectionnement du Conservatoire des Écoles Royales d'Arts et Métiers de Paris (1828), and of the Societé Française de Statistique Universelle (1833); he was President of the Societé d'Encouragement pour l'Industrie Nationale (1833), of the Jury of the National Exposition (1834 and 1844), of the Counseil d'Administration du Chemin de Fer de Sainte-Etienne à Lyon (1845), and of the Societé de Secours des Amis des Sciences. He was elected deputy for l'Yonne at the Grand Couseil (1827) and deputy for the districts Sens and Joigny (1830). In 1814 he was nominated Chevalier de la Légion de Honneur, promoted to Commandeur in 1837, and to Grand Officier in 1842. He was given the title of Baron in 1825 and in 1832 he was nominated Peer of France.

Thenard was appointed member of large number of foreign scientific organizations: Erfurt Academy (1811), Berlin Academy (1812), Science Society of Halle and Saale (1817), Naples Academy of Sciences, Munich Royal Science Society (1819), Academy of Sciences and Arts of Lucques (1820), Imperial Pharmaceutical Society of Saint Petersburg (1820), Royal Society of Sciences of Madrid (1821), Royal Society of Stockholm (1821), Royal Society of Edinburgh (1823), Academy of Sciences of Göttingen (1830), Medical and Botanical Society of London (1828), etc., etc.

Thenard is credited with over one hundred and fifty publications; his book *Traité de Chimie Élementaire Théorique et Practique* (five volumes, 1814-1816)[7], went through six editions and was translated to Spanish and German.

Many of the most important French scientists of the epoch studied under Thenard, among them we can mention François Ernest Ballard (1833-1894), Antoine Bussy (1794-1882), Auguste Cahours (1813-1891), Jacques Joseph Ebelmen (1814-1852), Edmond Frémy (1814-1894), Jules Jamin (1818-1886), Théophile-Jules Pelouze (1807-1867), Victor Regnault (1810-1878), and Henri Saint-Claire Deville (1818-1881).

As a suitable final remark we can mention that when Gustave Eiffel (1832-1923) built his famous tower in 1889, he decided to honor 72 distinguished French scientists by putting their names in the structure. This 'invocation of science", as Eiffel called it, reflected his worry over accusations that the tower was useless and waste less. There are eighteen names per side of the tower, all positioned just below the first platform of the structure, on the outside. The letters in the names are 60 cm high. Thenard's name is located on the third façade, opposite the Military Academy.

Thenard's last years were full of misfortune, with most of his family passing away in a very short period of time. First, his mother-in law passed away, then his devoted wife, his youngest son, followed by a brother, sister, and nephew. Thenard passed away on June 21, 1857, at the age of eighty, leaving one son alive.

Scientific activities

Thenard was a many-facet scientist; his principal contributions were the isolation of boron, the synthesis of hydrogen peroxide, and potassium amide, the manufacture of synthetic ultramarine blue, the preparation of very pure nickel, and the development of a new analytical method for the analysis of vegetable and animal matters. Several of his contributions were done in collaboration with Joseph-Louis Gay-Lussac (1778-1850).

In what follows we describe the principal aspects of his scientific work.

1. *Sebacic acid* (decanedioc acid)[8]

According to Thenard all the papers published about sebacic acid were related to proving that the product of the distillation of a fatty material contained an acid, very volatile, pungent and suffocating that could not be breathed without danger. Thenard demonstrated that although fat distillation yielded an acid that was actually solid and odourless, contained acetic acid, and was not contained in the odour of distilled fat. In addition, this compound was a new acid, up to that time unknown.

Thenard distilled a large amount of pork fat, treated it several times with hot water and subjected it to three different treatments to separate the new acid. For example, addition of lead acetate gave a flaky precipitate that he separated and dried and then heated it in the presence of sulphuric acid, The resulting liquid was not acid and had a supernatant melted product, similar to fat, which he separated, washed carefully and put it to boil with water. The solid dissolved completely in water, and on cooling it deposited crystalline needles, soft, acid in character and having very particular characteristics. In order to verify that they were not the results of the action of sulphuric acid, he treated the distilled fat with water, filtrated it, and then evaporated the liquid. The resulting product was again the same needles. He also added lead acetate to the liquor and separated *sebate de plomb* (lead sebacate), that the treated as before with sulfuric acid.

Afterwards, he proceeded to study the properties of the acid: It was odourless, had a slight acid taste, it melted like a fat, it tinted strongly litmus, and was very soluble in cold and hot water, and in alcohol from where it also crystallized in small or large needles. The acid precipitated lead acetate and nitrate, silver nitrate, mercury acetate, and nitrate, it neutralized alkalis forming soluble salts, and did not produce turbidity in suspensions of calcium hydroxide, baryte and strontia.

He then developed a method to separate sebacic acid from the acetic acid by treating the distilled fat with potassium hydroxide and drying completely. The solid phase was then treated with an acid (sulphuric, or phosphoric), followed by distillation. The distillate had all the characteristics of acetic acid.

Thenard closed his memoir indicating that be believed the procedure he had developed would also serve to show that the same acid was present in other fatty materials, such as human fat, beef marrow, and tallow.

2. *Zoonic acid*[9]

In 1798 Berthollet had distilled flour gluten, brewer's yeast, meat, and bones and obtained a new acid that he had named *acide zoonique* (zoonic acid). He believed that zoonic acid was the product of distillation of all animal matter.[10] He had also determined some of its properties, for example, it had a smell similar to that of roasted meat, was liquid at room temperature, boiled at the temperature of boiling water, tinted red litmus paper, it acted on alkaline carbonates with effervescence, and formed soluble salts with barite, potassium hydroxide, sodium hydroxide, strontia, calcium carbonate, and ammonia. It precipitated lead nitrate and mercury acetate and decomposed when heated, depositing carbon.

Fourcroy requested from Thenard to repeat Berthollet's experiences very carefully in order to verify Berthollet's findings. Thenard prepared several litres of the distillate and put the compound through a large number of tests that convinced him that it was not a new material, as claimed by Berthollet, but simply impure acetic acid, containing animal matter, which communicated to the solution the property of precipitating different metallic salts, particularly those of lead.

3. *Fermentation*[3]

Thenard did some research on the subject of alcoholic fermentation and concluded that all sugary juices, in the process of spontaneous fermentation, deposited a substance which resembled beer yeast, and which had the power of fermenting pure sugar. He believed that this yeast was *animal* in nature, since it contained nitrogen and yielded ammonia on distillation. His studies of the yeast used to ferment pure sugar showed that it underwent a gradual change and that at the end it was reduced to a white material that contained no nitrogen and did not react with sugar.

Louis Pasteur (1822-1895) quoted Thenard's analysis of the fermentation process in his well-known memory about alcoholic fermentation.[11] Eventually Pasteur got into a bitter dispute with Thenard's son, Paul, regarding a patent taken by Pasteur on the preservation of wines by the application of heat.[12-14]

4. *Bile*[15]

In his study on the nature and properties of bile Thenard remarked the difficulties facing research on materials of animal origin, not only because of their complicated nature but also because they emitted putrid and dangerous emanations and were foul smelling and repugnant. Among the many results obtained in the past were those claiming that bile contained an alkali, some type of sugar, an oily matter, and that is was a soap-like material composed of soda and milk sugar. Thenard decided to study in detail the properties and composition of the bile of ox, easily obtainable in large quantity. This type of bile had a green-yellow color; it had a slight sweet bitter repugnant taste, and smelled like heated meat. It had a specific gravity of 1.026 and contained about 90% weight water. Thenard distilled bile under different conditions, to total dryness, at high and low temperatures, and described the characteristics of the solid residue and distillate. His results indicated that bile contained less than 0.5 weight percent of soda, an amount that was too small to dissolve the solid residue left after distillation. Hence he concluded that it bile contained another substance of alkaline nature, which he then tried to isolate, by treatment with alcohol, ether, and a variety of saline solutions. Using a solution of lead acetate he succeeded in isolating a substance having a bitter, acrid, and slightly sweet taste, which he named *picromel* that was capable of dissolving the solid resin left after distilling bile. His final result indicated that bile was a compound of water, resin, picromel, a yellow albuminous substance, sodium carbonate, sodium chloride, sodium sulfate, sodium phosphate, calcium phosphate, and iron oxide.

5. *Ethers*[16-18]

The term ether applied to all volatile liquids made by distilling mixtures of acids and alcohols. It was known as a general reaction and many types of ether were prepared from the important acids. Five species were distinguished at the time, sulphuric ether, nitric ether, muriatic ether, acetic ether, and phosphoric ether (In today terms, we know that some of these ethers are actually esters). It was believed that the acid entered the composition of the ether and hence their names. All shared the common properties of being inflammable volatile liquids with a characteristic smell. In his first memoir on the subject[16] Thenard reviewed the information available about ethers and pointed out that it was not known if they were homogeneous in composition or not, the recommended method for their preparation, and the theory behind their formation. He then proceeded to prepare all the known ethers and to make a systematic study of their properties. He prepared nitric ether by reacting nitric acid with alcohol in a retort and studied the properties of the liquid and gaseous phases produced. The liquid phase was very acid and distilled in the presence of potassium hydroxide it yielded distinct fractions: (a) an ethereal liquid, (b) an alcoholic liquor and, (c) water. The remaining residue contained potassium nitrite and acetate. Similarly, the original liquid phase could be neutralized with lime and deposited a solid phase containing the calcium nitrite and acetate. Berthollet measured the vapor pressure of the neutral nitric ether and found it to be 0.73 cmHg at 21^{0}C. At the same temperature the vapor pressure of sulphuric ether was 0.46 cmHg. Thenard also measured the density of the gas phase produced by the thermal decomposition of the ether (0.08930 gram/liter) and determined. An elementary analysis of the ether indicated that it its percentage composition was nitrogen, 16.41; carbon, 39.27; oxygen, 34.73; and hydrogen, 9.59.

In another publication[17] Thenard reported on the preparation and properties of muriatic ether (ethyl chloride), particularly because some assumed that it was simply a mixture of the acid and the alcohol while others believed that it was a compound. Thenard showed that his ether did not contain free acid because it did not affect litmus paper, violet syrup, and a solution of silver nitrate.

In a following publication[18] Thenard studied the reaction between alcohol, metallic chlorides, oxygenated muriatic acid (chlorine), and acetic acid, as an alternative to produce the corresponding ether. Metallic chlorides, particularly that of tin, yielded essentially the same product as the reaction between alcohol and muriatic acid. Chlorine was prepared by reacting sodium chloride with sulphuric acid and manganese dioxide, as suggested by Scheele. Reaction with alcohol yielded a white oily substance, which was very soluble in alcohol and insoluble in water, smelled like mint, was heavier than water but more volatile, and was definitely not ether. Similarly, Thenard proved that acetic ether was truly a compound between the alcohol and acetic acid that released acetic acid when burned, and that treatment with potassium hydroxide yielded alcohol and potassium acetate.

Thenard summarized his findings by stating that none of the ethers had the properties of the corresponding acids, but each one when boiled with alkali regenerated the original alcohol and the acid. He classified the ethers into three classes; (a) those not containing the acid, an example were the common ether, which could be prepared from alcohol, and acid such from sulfuric, phosphoric, or arsenic (today, esters), and could be represented as a combination of olefiant gas (ethylene) and water; (b) ethers containing the radical of a hydroacid; these ethers could be prepared from alcohol and hydrogen chloride or iodide and could be represented as a combination of olefiant gas plus acid; and (c) ethers containing an oxyacid; these ethers could be prepared from acetic, nitric, benzoic, oxalic, and citric acids, and be represented as a combination of alcohol with the oxyacid.

6. *Nickel* [19]

According to Thenard, in spite that nickel was known for more than fifty years and had been the subject of many researches, it was still the issue of much discussion. Some regarded it as a metal of special nature; because of its magnetic properties others believed that is was actually impure iron; because of the blue colour of its oxide in its ammonia solution thought it to be copper; and finally others believed it was actually an alloy of arsenic and cobalt, because these two metals were always present in the mined where nickel was found. According to Thenard the reason for this uncertainty was the fact that it was very difficult to obtain pure nickel, and in particular, to separate it from cobalt, arsenic, and iron.

In his memoir[19], Thenard reported the experiments he had performed to separate nickel from the impurities present in the mineral that was available to him (iron, cobalt, bismuth, copper, arsenic, and sulfur). Eventually he was able to separate a sufficiently large sample of the metal to study its properties, particularly the ones that had originated the initial discussion. Thenard found that the magnetic properties of nickel, as tested with magnetized needles, were very similar to those of iron. He prepared an alloy of nickel with arsenic and found that its was fragile, grained, easy to melt, had no attracting powers, and that 50% weight of arsenic were enough to mask the magnetic properties.

Thenard studied the oxygenation of different acid and oxides, for example hydrogen chloride, nitric acid, sulphuric acid, and phosphoric acid[20-22], and studied their reactions with mercuric oxide, silver oxide, metals such as silver, iron, copper, bismuth, lead and platinum.

7. *Hydrogen peroxide* [23-27]

Thenard discovered hydrogen peroxide by a combination of good sense and luck. He told about the discovery to his son Paul as follows[3]: He was giving a class at the Sorbonne about salts and said the in order the metals join with acids it was not enough that they be oxidized first should be so only to a certain degree. An oxide containing too much oxygen lost a large part of its affinity for an acid, or would simply not combine at all. As examples he mentioned the peroxides of manganese, lead, tin, antimony, potassium and sodium. He was to include barium peroxide in his list when he remembered that the pertinent experience had not been performed. When the lecture was over he asked his Jean-Pierre Barruel (1780-1883) for a sample of oxygenated baryte. Thenard pulverized the compound and in order to accelerate the preparation he added a little water, a solution of hydrogen chloride, and a piece of ice that was at hand from his lecture. He continued to added pieces of the solid and noted, to his surprise, that it dissolved without effervescence. Thenard left the preparation and when he returned to give another lecture he noted that small globules were attached to the walls of the vessel, similar to the ones in a glass filled with champagne. Out of curiosity he hated the container and noted the disengagement of a large number of bubbles. He introduced a burning match into the gas phase he noted that instead of ignition the flame burned more vividly: the gas was oxygen and not hydrogen!

Thernard proceeded then to determine the properties of the new compound and reported that it was colorless and odourless, that if froza and vaporized in vacuum without decomposing but atmospheric pressure it released oxygen when heated by boiling water, he also found that hydrogen peroxide contained one part more of oxygen than pure water and that many organic materials such as fibrin, lung, skin, blood vessel and spleen tissues, were able to release oxygen without decomposing, the same as platinum, gold, and silver did. On the hand, organic materials such as urea, liquid or solid albumin, and gelatine liquid did present this characteristic. Hydrogen peroxide was also decomposed by charcoal, by lead dioxide and the oxides of platinum and silver. He also commented that putting in contact hydrogen peroxide and silver oxide both decomposed releasing a large amount of heat, although in theory the effect have been a cooling one. Even though he could not understand where was the heat coming, from, he suggested the possibility of an electrical origin. He also asked the question, without answering it as to why materials so different in nature had the property of decomposing hydrogen peroxide.[24-26]

On a later publication Thenard gave detailed instructions of how to prepare hydrogen peroxide, starting from barium nitrate.

Thenard thought that because the analogy that existed between oxygen and sulfur, hydrogen sulphide would behave like water. He found that gold, platinum, iridium, and other elements decomposed hydrogen polysulfide into sulfur and hydrogen sulphide, but surprisingly, that potassium sodium, and ammonia that had a strong affinity for hydrogen sulphide and sulfur and should combine with hydrogen polysulfide, decomposed it in the same manner as the elements mentioned before. Unfortunately, the pernicious action of polysulfide on the respiratory system was unknown at the time, and as a result of it Thenard became seriously ill. This poisoning affected his health until his death.

8. Catalysis

Thenard's work on the decomposition of hydrogen peroxide by metals and certain organic materials may be considered the origin of this interest in catalysis (without knowing the meaning of the phenomena). Johann Wolfgang Döbereiner (1780-1849) had recently discovered the remarkable property that platinum sponge had of causing the reaction of oxygen and hydrogen to produce water at room temperature and that the heat of the reaction was sufficient to make the sponge incandescent.[28] Thenard was astounded to see that the same material that decomposed water peroxide by simple contact was able to induce the reaction between oxygen and hydrogen. He understood that in order to understand the phenomenon he required the help of some one with a strong background in physics, and for this reason he requested the collaboration of Pierre-Louis Dulong (1785-1838). The results of this collaboration were described in two memoirs they published together. Thenard and Dulong found that other materials such as the sponges of palladium, rhodium, and iridium, presented the same characteristics as that of platinum. All these compounds lost this characteristic under conditions that Thenard and Dulong determined. In addition, compounds such as osmium, silver, charcoal, pumice stone, porcelain, glass, and rock glass acquired it at high temperatures.[29, 30]

Iridium, presented the same characteristics as that of platinum. All these compounds lost this characteristic under conditions that Thenard and Dulong determined. In addition, compounds such as osmium, silver, charcoal, pumice stone, porcelain, glass, and rock glass acquired it at high temperatures.[29,30]

Collaboration with Gay Lussac

Thenard carried out a considerable amount of research in collaboration with Gay-Lussac in the period 1808 to 1811. Their joint efforts are reflected in about twenty joint scientific papers and a book.[31] Although they came from completely different social backgrounds they had many common interests, which become stronger when they became part of the *Societé d'Arcueil*, founded by Claude-Louis Berthollet (1748-1822) and Pierre-Simon Laplace (1749-1827).

Upon hearing about Davy's discovery of potassium (1807) Gay-Lussac and Thenard joined efforts to do research on the new element. After many intents, they succeeded in preparing potassium and sodium by alternative methods, in particular, heating the appropriate alkali at high temperatures with iron filings.[32,34] Gay-Lussac and Thenard carried the reaction in a gun barrel and the vapor of the metal was condensed in a receiver attached to the barrel with a cement lute. Compared to Davy's electrolytic procedure, their method of preparation had the advantage of preparing the metal in large quantities (about 25 grams per batch), at a comparatively low cost, and thus allowing an easy mean to study its properties. Gay-Lussac and Thenard found that the specific gravity of potassium was 0.874 (Davy had reported 0.6) and that it caught fire in contact with water and generated potassium hydroxide. Potassium combined easily with phosphorus, sulfur, and a large number of metals, particularly with iron and mercury. The reaction with phosphorus and sulfur was highly exothermic and luminous. Addition of the reaction product with phosphorus to water yielded phosphine, while the one with sulfur formed a sulfate and hydrogen sulfide. Heating potassium with hydrogen yielded the gray solid potassium hydride; heating it with ammonia produced potassium amide, KNH_2, the first amide of a metal ever prepared; when this amide was heated strongly, part of the ammonia was regenerated leaving a solid residue of K_3N.

Gay-Lussac and Thenard also found that the amalgam of sodium and potassium was liquid at room temperature.

The most interesting reactions were with gases. Potassium burned lively with oxygen at room temperature, yielding potassium hydroxide. When in contact with atmospheric air, at room temperature, it first took a blue color; with agitation it melted yielding a brilliant liquid, which afterwards caught flame converting into potassium oxide. It did not absorb nitrogen and did not react with it. At high temperature it reacted with a substantial amount of hydrogen and transformed into a whitish gray solid, which yielded hydrogen when contacted with mercury or water. Other reactions studied were with phosphine, hydrogen sulfide, arsine, hydrogen fluoride, nitric acid, chlorine, sulfur dioxide, carbon dioxide, carbon monoxide, ammonia, etc.

Their research on the reactions of potassium led to the discovery and synthesis of many new compounds. Treatment of boracic acid with potassium at high temperatures led to the isolation of a new element, which they named *bore* (boron) for the radical of boric or boracic acid.[35] Gay-Lussac and Thenard noted the similarity of boron properties to those of carbon, phosphorus, and sulfur; boron would form borides similar to carbides, etc.

Their success in isolating the radical of boric acid encouraged Gay-Lussac and Thenard to try to find a way to isolate other radicals. Their efforts were thwarted by practical difficulties, and in the case of fluorine[36] them and a succession of various chemists fail to isolate the element until Henri Moissan (1852-1907; 1906 Nobel Prize for Chemistry) did it in 1886.[37]

Early analyses of organic matter were based on its decomposition by heat into charcoal and water, which were collected and weighted, and into gaseous products which were analysed in a eudiometer. In 1810 Gay-Lussac and Thenard announced that they had successfully applied potassium chlorate to the analysis of sixteen vegetables and four animal substances.[38] The exchange of combustion by oxidation with potassium chlorate was a significant step forward since it allowed chemists to analyze any organic substance and not simply inflammable ones. Nevertheless, the experimental procedure was cumbersome and dangerous because potassium chlorate was too reactive, producing over a short period of time large volumes of gases, which shattered the apparatus. These difficulties were later avoided by finely grinding the organic substance, mixing it with potassium chlorate, and then adding it to the apparatus in the form of pellets of weighed amounts. Their apparatus consisted of a vertical tube made of thick glass, closed at the bottom and fitted on the upper end with a stopcock, which contained a cavity large enough to hold a pellet. The bottom of the tube was strongly heated by a charcoal fire. A pellet would be placed in the stopcock cavity, the stopcock turned and the pellet would fall into the tube, resulting in instantaneous combustion. This procedure would be repeated until all the air in the apparatus was driven out and replaced by an atmosphere, which would be identical to the atmosphere in the apparatus at the end of the experiment. A weighed quantity of pills would then be gradually added and the gases generated (carbon dioxide and excess oxygen) were collected in a jar over mercury by means of a side tube. The amount of CO_2 present in the gas was determined by absorption in potassium hydroxide while the oxygen content was determined by addition of hydrogen and detonation of the mixture. The amount of oxygen released by a given weight of potassium chlorate was determined by operating the apparatus in the absence of organic matter. The difference between the latter and the amount of oxygen in the collected gas indicated the amount of oxygen, which had been transformed into water and CO_2; the amount of CO_2 was known and therefore the amount of water formed could be calculated.

The above operating procedure was applicable only to vegetable substances. Animal substances released nitrogen gas and its amount was estimated by operating the equipment with an insufficient amount of potassium chlorate. This prevented the formation of nitrogen oxides.

The procedure of Gay-Lussac and Thenard overcame the two main two difficulties, which were present in all previous methods: (a) to achieve complete combustion and, (b) to perform the combustion in closed vessels without their shattering. Anyhow, the procedure could not be used for liquid or volatile substances.

Gay-Lussac and Thenard analysed sugar, gum arabic, starch, milk sugar, and oak and beech wood, and found that they all contained hydrogen and water in the proportion required to form water (carbohydrates), and that they were neutral. They also analysed the five acids mucic, oxalic, tartaric, acetic, and citric, and found that in them the ratio of oxygen to hydrogen was larger than that needed to form water. Analyses of resins, wax, olive oil, and copal indicated that in these materials hydrogen was in excess above oxygen.

Based on all their analytical results Gay-Lussac and Thenard reaches the following conclusions[37] (a) a vegetable substance is always acid when oxygen is to hydrogen in a relation greater than that found in water, (b) a vegetable substance is always resinous, oily, or alcoholic, when oxygen is to hydrogen in a relation less than that found in water, and, (c) A vegetable substance is neither acid nor resinous, and is analogous to sugar, gum, starch, sugar, or milk, to the ligneous fibre, to the crystallisable principle of the manna when oxygen and hydrogen are present in just the proportion to form water.

The work of Gay-Lussac and Thenard suggested that vegetable substances are composed of carbon and water, and animal substances of carbon, water, and ammonia. Animal substances with exactly the proportion to form water and ammonia were analogous to the sugar class; those with an excess of oxygen were animal acids analogous to vegetable acids; and animal fats, which have an excess of hydrogen over that needed to form water and ammonia were analogous to the class of resins, vegetable oils, etc. In other words, animal and vegetable substances could be classified into three great orders. The classification was based on composition and *not* on properties.

At the beginning of the nineteenth century chlorine was known as *oxymuriatic acid* or *oxygenated muriatic acid,* since it was thought to be a compound of oxygen and muriatic acid (HCl). This belief originated on the way the acid was prepared: heating muriatic acid with a substance such as manganese dioxide, which contained a large percentage of oxygen. In addition, it was known that an aqueous solution of oxymuriatic acid released oxygen bubbles when it was exposed to sunlight. Moreover, many substances burned brilliantly in oxymuriatic acid and oxygen was the only known supporter of combustion. These and other facts have lead to the conviction that oxymuriatic acid was a compound containing loosely combined oxygen.

Gay Lussac and Thenard thought that muriatic acid the only one of the gases which contained combined water and made a large number of experiments to determine if the latter was actually essentially to its intimate constitution.[39] In order to determine the quantity of water that could be extracted from the acid they first dissolved it in water and then added a solution of silver nitrate. From the analysis of the precipitate they determined that 27.151 grams of the acid contained 6.54 grams of water, or 0.240 of its weight. This result was confirmed by passing the acid over iron turnings or by reacting it with ammonia. Other reactions yielded some unexpected results. The sulfides of barium and calcium reacted with the acid only when wet and released large amounts of hydrogen sulfide. Phosphorus did not separate oxygen but combined directly with the acid. Oxymuriatic acid gas was not decomposed when passed over red-hot coal, although the latter was one of the best-known reducing agents. Sulfurous gas (SO_2), nitrous oxide gas, CO, and nitrous gas were able to decompose oxygenated muriatic acid only in the presence of water; no reaction took place if the gases were dry. Gay-Lussac and Thenard concluded that muriatic acid could not exist without water in the state of gas, and that only bodies containing hydrogen were able to decompose it.

The experimental results led Gay-Lussac and Thenard to doubt that oxymuriatic acid gas contained oxygen and to suggest that it may be an element: "In fact, oxygenated muriatic acid is not decomposed by charcoal, and it may be supposed, from this fact and those which are communicated in this memoir, that this gas is a simple body. The phenomena which it presents can be explained well enough on this hypothesis; we shall not seek to defend it, however, as it appears to us that they are still better explained by regarding oxygenated muriatic acid as a compound body."

The same memoir contains a pioneering contribution to photochemistry. Gay-Lussac and Thenard studied the influence of light on the reaction between chlorine and hydrogen (or ethylene) and realized that in the case where compounds were formed only slowly, it was due to the fact that light was 'added" in small amounts. When the solution was left for a long time to the action of the agent then large effects were achieved. The change in color of the gases enabled them to follow the course of the combination over several days in hazy sunshine, keeping meanwhile another mixture of the reactants in the dark as a control. In bright sunlight the gases inflamed with a very loud detonation, shattering the flasks used. Gay-Lussac and Thenard concluded that light was the cause of the decomposition of oxygenated muriatic acid when it was mixed with hydrogen or with compound hydrogen gases. The fact that CO did not react with the acid was another proof that it did not contained hydrogen.

Gay-Lussac and Thenard also prepared new compounds with chlorine, including phosphorus oxychloride ($POCl_3$).

It was left to Davy to prove unequivocally that chlorine was an element.[40]

Acknowledgment

The help of Mrs. Karine Barker, Librarian, Document Supply Department, Radcliffe Science Library, Oxford, in providing copies of hard-to-get documents is gratefully acknowledged.

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Bon Thenard

Figure 1: Louis-Jacques Thenard (1777-1857). (By permission of Edgar Fahs Smith Collection, University of Pennsylvania Library)