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BIBLIOGRAPHIC REVIEW

LOUIS HENRI FREDERIC MELSENS

Nicotine, potassium iodide, and sulfur compounds

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ABSTRACT

Louis Henri Frédéric Melsens (1814-1886) was a Belgian chemist, student of Dumas and Liebig, who showed the possibility of chlorinating an organic compound by hydrogen substitution; separated nicotine, determined its formula, and proved it was a powerful poison; discovered and described the composition and properties of sulfacetic acid, developed the synthesis of sulfuryl chloride by diverse procedures involving the direct reaction between SO_2 and chlorine. Melsens carried an extensive study on the possibility of using potassium iodide as an antidote to poisoning by mercury and lead; the basic idea was to try to stabilize the metallic compounds that the animal economy retained by associating them with a substance that the economy was able to eliminate easily. He took advantage of the fact that all the insoluble compounds formed by mercury salts found in animal economy were soluble in potassium iodide and that the body could eliminate easily. He studied the action of activated carbon on the partial solidification of a volatile liquid, the accompanying thermal phenomena, and proved that the wetting of a solid was accompanied by an increase in temperature. He developed an improved process for the saponification of fats, for the extraction of sugar with the help of calcium bisulfide, a very efficient lightning rod based on Faraday's electric cage, and analyzed a series of physical problems related with firearms and ballistics.

Keywords: activated carbon; nicotine; potassium iodide; sulfoacétic acid; sulfuryl chloride

RESUMEN

Louis Henri Frédéric Melsens (1814-1886) fue un químico belga, alumno de Dumas y de Liebig, que demostró la posibilidad de clorar un compuesto orgánico por substitución de hidrógeno; separó la nicotina, determinó sus fórmula y demostró que era un veneno poderoso; descubrió y determinó la composición y propiedades del ácido sulfo-acético; desarrolló la síntesis del cloruro de sulfurilo por diversos procesos basados en la reacción directa entre el dióxido de azufre y el cloro; y estudió la condensación del cloro mediante el carbón activado. Melsens llevó a cabo un extenso estudio acerca de la posibilidad de utilizar el yoduro de potasio como antídoto contra el envenenamiento por mercurio y plomo; la idea básica era estabilizar los compuestos metálicos que la economía animal retenía, asociándolos con una substancia que la economía eliminaba con facilidad. Para este efecto aprovechó el hecho que los compuestos insolubles formados por las sales de mercurio eran soluble en yoduro de potasio y que el cuerpo los podía eliminar fácilmente.

Estudió la acción del carbón activado en la solidificación parcial de un líquido volátil, los fenómenos térmicos asociados, y demostró que el mojado de un sólido estaba acompañado por un aumento de la temperatura. Melsens desarrolló un proceso mejorado para la saponificación de las grasas, un proceso para la extracción de azúcar mediante bisulfuro de calcio, un pararrayos muy eficiente basado en la jaula eléctrica de Faraday, y estudió una serie de problemas físicos relacionados con armas de fuego y la balística.

Palabras clave: ácido sulfo-acético; carbón activado; cloruro de sulfurilo; nicotina; yoduro de potasio.

INTRODUCTION

Life and career

The information about the early life and education of Louis Melsens (Figure 1) is very scarce (De Heen, 1893; Henriot, 1958). He was born on July 11, 1814, in Louvain, Belgium. After some basic education from his mother, he entered the Collège de Louvain. Upon graduation, his father, a local merchant, wanting his son to follow his steps, sent him for an apprenticeship in the commercial house of the brothers Josson, in Anvers. After realizing that he did not have the minimum aptitudes for this profession, Louis returned home and under his mother encouragement, he moved to Paris to study chemistry and work in the laboratories of Jean-Baptiste André Dumas (1800-1884) at the Sorbonne. There he published his first important paper proving that it was possible to chlorinate an organic compound by substitution (Melsens, 1840). After four years he moved to Germany to continue his chemical education at the university of Giesen, where he came into contact with Justus von Liebig (1803-1883) and received a Ph.D. in natural sciences 1851. After his return to Belgium he was appointed to the chair of chemistry and physics at the École de Médicine Vétérinaire de l'État in Kurenghem, near Bruxelles, and permanent examiner at the École Militaire (De Heen, 1893; Henriot, 1958).

Melsens passed away in Brussels on April 20, 1886, after a successful academic and research career. In her testament (1900), his widow left the sum of 10,000 francs to the Division of Sciences of the Académie Royale des Sciences, des Lettres, et des Beaux-Arts de Belgique to establish the Louis Melsens Prize, to be awarded to a Belgian or naturalized Belgian author of the most remarkable work in applied chemistry or physics (De Heen, 1893; Henriot, 1958).

Melsens received many honors and awards for his contributions to science and technology. In 1846 he was elected correspondent member of the Académie Royale des Sciences, des Lettres, et des Beaux-Arts de Belgique (1848); in 1851 he was promoted to member, and in 1859 he was elected Directeur of the Class des Sciences. He was the first president of the Belgian Electrochemical Committee.

Melsens was a very versatile scientist who did research in a wide range of subjects: (a) chemistry, (b) physiology, (c) electricity, (d) pharmacy, and (e) gunpowder, ballistics, and weaponry, In addition to the subjects described in detail below, we can mention the presence of mannitol in avocado (Melsens, 1839), chlorination of organic compounds, including the transformation of chloroacetic acid into acetic acid and back into chloroacetic acid (Melsens, 1840, 1842, 1844a, 1873d), the acidity of gastric juice (Melsens, 1844b), the composition of cs (Melsens, 1844b), the determination of nitrogen in organic substances (Melsens, 1845a), formation of mercury bubbles in the process for obtaining silver by amalgamation (Melsens, 1845b), a new procedure for extracting sugar cane and beet sugar based on the use of calcium bisulfite (Melsens, 1849b, 1850, 1862), persistence of impressions in the retina (Melsens, 1857), gunpowder and mechanics of weaponry (Melsens, 1861, 1865, 1867, 1872b), the preparation of SO_2, some of its derivatives, and uses (Melsens, 1873ab), lighting rods (Melsens lightning conductor system) (Melsens, 1865de 1872a, 1883), etc.

Several of his findings were the subject of industrial patents, for example, an improved method for manufacturing sugar from cane and beet roots (Melsens, 1850), the fabrication of glucose (Melsens, 1855a), saponification of fatty materials by acidulated water (Melsens, 1855b), and improving alcoholic liquors by freezing (Melsens, 1873g).

Scientific contribution

Melsens wrote near 90 papers in the areas of chemistry, physiology, electricity, pharmacy, gunpowder, ballistics, and weaponry. A very detailed list appears in the paper by Pierre De Heen (1851-1915) (De Heen 1893).
Here we describe s few of his most important pieces of work.

Action of sulfuric acid on acetic acid

In 1843 Melsens carried on a large series of experiments to confirm certain theoretical ideas regarding the constitution of some organic acids suggested by Dumas, his mentor (Melsens, 1843b). Dumas had proposed that acids such as tartaric and citric were polybasic because they were formed by the combination of two or more acids, each one mono or polybasic. Thus, tartaric acid should be considered to be formed of oxalic acid and of acetic acid, and sulfobenzoic acid of sulfuric and benzoic acids. Melsens went on to test the possibility that the reaction between acetic acid and sulfuric acid would produce a conjugated acid, which would be related to acetic acid as sulfobenzoic acid was to benzoic acid. He also speculated that the resulting acid would have the properties of tartaric acid where oxalic acid had been replaced by sulfuric (Melsens, 1843b).

Melsens added anhydrous sulfuric acid drop-wise to acetic acid and noted that after some time the odor of acetic acid disappeared completely and the resulting liquid became colorless or slightly yellow. This liquid, added slowly to water at 0^0C, decomposed completely into sulfuric and acetic acids, but did not if the resulting liquid was heated to 60^0 to 75^0C, kept thus for some days, and then added to water. Now the resulting acid, which Melsens named *sulfacetic acid*, reacted with barium and lead carbonate to produce soluble salts, which were completely different for the pertinent acetates. The acid was easily separated from its lead salt by means of hydrogen sulfide. According to Melsens, sulfacetic acid was a solid crystallizing as silky needles, highly deliquescent, soluble in water and alcohol, and forming well defined salts with oxides. Salts of calcium, lead, or silver did not precipitate the aqueous solution. An elementary analysis of the crystallized acid and the one effloresced in vacuum indicated that their respective formulas were $C_3H_4O_3$, S_2O_5, $2H_2O$, 3aq and $C_3H_4O_3$, S_2O_5, $2H_2O$, 2aq. The results indicated that sulfacetic acid was able to saturate two base equivalents, Melsens accepted that the sulfur was present in the acid half in the state of SO_2 and in the other half as sulfuric acid (SO_3), and that the SO_2 had replaced the hydrogen lost by the acetic acid during the reaction (Melsens, 1843b). Melsens prepared the potassium, barium, lead, and silver salts of the acid and determined their respective amount of crystallization water. He also reported that passing a stream of HCl through an alcoholic suspension of silver acetate produced silver sulfovinate, which proved that the acid was dibasic (Melsens, 1843b).

In a following paper (Melsens, 1844d) he added more information about sulfacetic acid. He remarked that ordinary sulfuric acid reacted with acetic acid at room temperature, releasing CO_2 and SO_2 in variable proportions. Using 20 or 30 parts of sulfuric acid per one of acetic generated a gas mixture containing equal volumes of both gases. When acetic acid was treated with an excess of fuming sulfuric acid of Nordhausen, the mixture heated up and remained for some time without reacting. On heating it began to release CO_2 pure, and if it was stopped on time and neutralized with barium carbonate, the product was now organic salt containing sulfur. With due precautions it was possible to obtain the combination of both acids without release of gas. If the mixture was then neutralized with barium carbonate, it yielded the insoluble sulfate of the acetate and sulfacetate. Additional experiments indicated that the most efficient method for preparing sulfoacetic acid was to react cold acetic with anhydrous sulfuric acid, followed by neutralization with barium carbonate, decomposition of the later with sulfuric acid, precipitation with silver oxide, and decomposition of the resulting salt with hydrogen sulfide (Melsens, 1844d).

According to Melsens, crystallized sulfacetic acid melted at about 62^0C; heated to about 160^0C it acquired the characteristic odor of caramel; the decomposition was complete at about 200^0C. Sulfacetic acid had a very acid taste, similar to tartaric or citric acids; it reddened litmus paper and decomposed carbonates. Melsens described the preparation and properties of the sulfacetates of potassium, barium, silver, and lead, and of silver sulfacetovinate (Melsens, 1844d).

Nicotine

In 1843 William Christopher Zeise (1799-1847), a Danish chemist, analyzed the smoke of tobacco and reported that the principal constituents were an empyreumatic oil, CO_2, ammonia, butyric acid, a hydrocarbon, and resinous compounds (Zeise, 1843). In his experiments he collected the smoke of a smoking pipe with a Brunner aspirator (Brunner, 1836) (a predecessor of the present water jet pump) and made it flow through (1) diluted sulfuric acid, where he gathered a brown pulverulent material, insoluble in alcohol and similar to the one obtained during the distillation of tar with sulfuric acid; (2) a solution of KOH, where he collected CO_2, free ammonia, butyric acid, and an empyreumatic oil containing, by weight, 71.0% carbon, 11.8 hydrogen, and 17.2% oxygen; and (3) an ice-cooled glass tube filled with glass fragments, where he detected the same products obtained during the dry distillation of tobacco in an iron retort. Zeise mentioned that the butyrates extracted from tobacco, when not too diluted, gave a green precipitate with cupric chloride and a white one with basic lead acetate, mercurous oxide, or silver nitrate. Curiously, he did not report the presence of nicotine, although he mentioned that he had detected nitrogen in quantities below 3% (Zeise, 1843).

Melsens wrote that he had been working on the question of the analysis of tobacco smoke for several years and was surprised that Zeise had missed the presence of nicotine, a component present in substantial amounts (Melsens, 1843a). In the past he had investigated the composition of the smoke trying to understand the reason for the alarming symptoms experienced by people during the first time they had smoked, and the strong repulsion shown by animals to the odor of tobacco. He had also noticed that insects were rapidly asphyxiated in a smoke atmosphere, and that during the use of German pipes, an extremely acrid brown liquid accumulated in the piece. He now decided to experiment on tobacco leaves from Virginia, known to produce extremely strong cigarettes. His apparatus was very similar to that of Zeise; the leaves, grossly cut, were put in a large porcelain pipe, burned without any additional preparation, and the resulting smoke was contacted successively with water and with two solutions of sulfuric acid of different concentration. The whole apparatus was connected to a large Brunner aspirator to force the gas through (Melsens, 1843a).

Melsens noted that the smoke that condensed in the first flask produced brown alkaline water, having a nauseous odor, effervescing with acids, and releasing ammonia in contact with bases. The liquid was muddled with a considerable amount of soft empyreumatic oily products, completely soluble in alcohol. It was also extremely poisonous; half a spoon was enough to kill a dog instantly. The smoke that condensed in the vessels holding sulfuric acid produced a darker, almost black solution, containing tarry resinous substances. The sulfuric acid neutralized the odor of ammonia volatile products (Melsens, 1843a).

Melsens used the procedure suggested by Jean-Augustin Barral (1819-1884) to separate the nicotine contained in the first vessel (Barral, 1842). The condensation products retained in this vessel were treated with acid and then filtrated to eliminate the tarry matter. The filtrate was neutralized with chalk and then distilled. The alkaline liquid that passed over was neutralized with a slight excess of acid and concentrated by evaporation. The tarry material that precipitated was eliminated by filtration and the brown filtrate treated with KOH, ether, distilled again, etc. h could possibly occur in the living economy, even metallic mercury itself, were soluble in KI and the presence of the organic substances of the body did not hinder these reactions. Mercury absorbed and retained by the body probably forming within it insoluble compounds, either with the organic or inorganic materials of the body or with both conjoined. According to Melsens the possible combinations could be divided into four main groups: (a) those of corrosive sublimate ($HgCl_2$), whether in its simple state or as modified by the animal substances of the economy, such as albumen; albumen and the materials of the brain; gelatin; the nitrogenous extractive matter of the blood, of muscle, of the urine, etc.; albumen, fibrin, muscular fiber, gelatin; and matters of the bile; (b) mercurial soaps; (c) mercury phosphates; and (d) metallic mercury All these compounds were soluble in alkaline or neutral pure KI dissolved in one of the liquids of the body; (3) KI traversed the economy very rapidly; alkaline iodides had a strong tendency to join with metallic iodides, free or associated with organic materials. Was it probable that the elimination of an alkaline iodide was accompanied by the elimination of double or triple compounds with the metallic iodides (something easily carried on in the laboratory)? To test this point Melsens swallowed 44 g of KI in eight days, and afterwards tested his urine with starch, acid, and chlorine; on the second day he no longer detected the presence of KI; (4) it was not possible to give directly the same proofs for solutions of lead compounds. He could only mention that lead iodide was soluble in alkaline liquids and had a clear tendency to combine with alkaline iodides; (5) lead colic occurred particularly after second wash water. Melsens believed that lead was present in the living body in the form of a sodium plumbate; and (5) KI could probably be replaced by alkaline chlorides and bromides, for treating diseases caused by metallic poisons (Melsens, 1849a).

The following sections were devoted to cases of lead poisoning. Melsens described the symptoms exhibited by four human subjects and one dog, and remarked that treatment with KI was successful in each one. Some of the important observations were as follows: (1) Sulfuric acid and sulfates were inappropriate antidotes to chronic poisoning by lead salts or compounds. Lead sulfate of lead was a slow and sure poison capable of killing vigorous dogs in twenty or thirty days. Magnesium sulfate could possible act as an antidote on the unabsorbed portion of a soluble lead salt; (2) the intoxication effects of lead sulfate were not proportional to the quantity of poison administered; (3) lead sulfate obtained by double decomposition, washed and ground, was as poisonous as that obtained by precipitation from a soluble salt of lead with sulfuric acid; (4) sudden treatment of a dog that had been for some time under the poisonous influence of lead sulfate, with a large amount of iodide of potassium would kill him. Nevertheless, a dog that was administered simultaneously lead sulfate and KI, would suffer no harm. Potassium iodide could be employed therefore as a prophylactic; (5) administration of KI in the case of advanced poisoning would probably aggravate the morbid symptoms; and (6) lead iodide acted on the living economy on a similar form as lead sulfate or carbonate, although it did it more rapidly (Melsens, 1849a).

The following sections described the treatment of several gilders and of workers with mercury. Administration of KI led to a clear improvement in their state and proved that in the cases were mercury was absorbed daily on small doses, the salt had not only curative power but also prophylactic ones (Melsens, 1849a). Further experiments showed that administration of KI rendered medical treatment or poisoning by certain salts of mercury more active, and could lead to serious accidents. Melsens found that if the same doses of calomel were given to two dogs, and KI given to one at the same time, the latter would die first, particularly if the doses of the two salts were large (Melsens, 1849a).

In following papers in the domain of experimental physiology, Melsens reviewed his previous findings and then described his procedure for preparing KI free of iodate. He recommended that before preparing the aqueous solution of KI to be used as antidote, the salt should be calcined in an iron recipient in the presence of a small amount of sodium carbonate or sulfide. The solution should contain 1 g of KI per 10 cm^3 of water and ought to be ingested together with the food or with ordinary non-acid beer or natural mineral waters. The presence of iodate should be avoided by all means because it was a potent poison, as shown by some of the experiences he had carried on with dogs (Melsens, 1865ab).

According to Melsens, the easy reduction of potassium iodate in solution, by reducing substances such as hydrogen sulfide, SO_2, and arsenious acid, indicated that this salt would certainly find in the organism a crowd of substances that would reduce it, totally or partially, by seizing its oxygen and leaving potassium iodide. The experimental evidence showed that potassium iodate in contact with fresh cold urine was rapidly partially reduced; with warm urine the process was even faster.

Melsens speculated that if the iodate was toxic, then it could, perhaps, become an important medicine having a double chemical role: it would first burn (oxidize) certain substances that the body eliminated as water, CO_2, and ammonia, and then pass into the blood as KI (Melsens, 1865ab). The following sections of this paper included a long description of poisoning by mercury, lead, and zinc, and the effects of KI on its treatment, as reported by diverse physicians (Melsens, 1865ab).

The fact that some soluble chemicals acted as poison antidotes and others as potent poisons, led Melsens to study the effect of both kinds of salts upon animal economy. His experiments, as shown below, led to the following proposition: “Two soluble salts which are without apparent mutual action, and which may be given separately to animals without producing any disturbance in the body, may, when administered together, act as a poison”. He proved his contention using potassium chlorate and potassium iodide, which were known to crystallize separately when dissolved together. It was also known that the mixed solution underwent no mutual decomposition at room temperature, on boiling, or under the pressure of 10 atmospheres at 185°C. Notwithstanding, when heated together in the dry state to about the fusion temperature of potassium chlorate, they decomposed violently with formation of potassium iodate. In addition, acidification of a solution led to the formation of free iodine and possibly iodic acid; electrolysis of the same solution liberated hydrogen at the positive pole while the liquor seemed to contain both iodine and iodate (Melsens, 1866abc).

Melsens conducted a series of experiments on animals. In one of them he administered to a dog weighing 11 kg, 7 g per day of potassium chlorate during one month and did not notice any negative effects. The same result was observed when the animal was given 5 g per day of potassium iodide for the same period. If, on the contrary, the animal was fed daily a mixture of 7 g of potassium iodide and 5 g of potassium chlorate, the animal languished and died about the twenty-fifth or twenty-eighth day. At the beginning of the experiment the dog weighed 16.5 kilos and at the moment of its death it weighed only 11.5 kilos. The experiment repeated on several dogs gave similar results. Post mortem examinations revealed changes similar to those observed by Melsens when potassium iodate of potash was administered, especially in the liver and intestines. Melsens believed that the mixture of the two salts could hardly be so active as the iodate alone, since both unchanged iodide and chlorate were found in the urine. He concluded that the mutual action of the two salts in the economy took place much easier than in chemical flasks; that is, many chemical changes, which took place in the animal system, could not be brought about under ordinary circumstances in the laboratory (Melsens, 1866abc).

The following paper described the results of a series of experiments devoted to prove the poisonous effects of potassium iodate. Melsens gave 2 g of potassium iodate (dissolved in water) per day to a dog weighing 9.6 kg and well supplied with food. Vomiting took place after the first administration; on the third day the vomit, containing pieces of bread, was tinged in patches of a violet-blue color as if a solution of iodine had been injected into the stomach. This phenomenon occurred on several succeeding days until the dog died weighing only 7.6 kg. Similar results occurred with a dog injected subcutaneously with 20 g of potassium iodate. Melsens remarked that although the constitution of potassium iodate did not seem to change when contacted for several days with pure albumin and fibrin obtained from a horse, the red blood globules disappeared rapidly and produced a seemingly limpid red garnet solution (Melsens, 1871a).

In additional notes on the subject, Melsens provided more details of the post mortem examination of animals killed by potassium iodate. It was clear that all the sanguineous system had been substantially affected. The cavities of the heart were full with non-coagulant blood, the blood of the arteries was full of brown blood rods, the brain was the site of a strong sanguine injection, all the vases were gorges of blood, etc. The digestive system was also the site of a violent inflammation, particularly the stomach and the colon (Melsens, 1871bc). These researches earned Melsens Montyon Prize of the Académie des Sciences de Paris and the Guinard Prize (10,000 francs) of the Académie des Sciences de Bruxelles.

Copper and lead in blood

In 1848 Auguste Nicolas Eugène Millon (1812-1867) read a memoire to the Académie de Sciences reporting his study about the normal presence of many metals in human blood, and the analysis of fixed salts in the fluid (Millon, 1848a). He wrote that when venous blood was dripped on three times of water and then the mixture introduced in a flask containing chlorine, the blood coagulated, turned brown, and then became a gray amorphous mass in which all the organization of the blood globules had disappeared. The organic materials were almost completely located in the portion coagulated while all the saline principles were in the liquid. Hence, this procedure allowed for a very simple method for determining the inorganic salts present in the blood. Millon evaporated the liquid to dryness, calcined it, and analyzed the residue, finding that 100 parts of the insoluble portion of this residue contained from 1 to 3 parts of silicic acid, 1 to 5 of lead, 0.5 to 2.5 of copper, and 10 to 24 of manganese. He then went on to determine if the copper and the lead were disseminated in the full blood, or like iron, it was concentrated in the blood globules. His results indicated that 1000 g of human coagulum (crassamentum) separated carefully from the serum, contained 0.083 g of these metals, while 1000 g of carefully separated serum contained only 0.003 g of the two metals. Millon commented that these three milligrams could be undoubtedly attributed to blood globules dissolved or suspended in the lymph (Millon, 1848a).

This memoir brought a very critical answer from Melsens (Melsens, 1848). He reiterated that in his work about the use of potassium iodide to fight the chronic affections originating from poisonous metals, he had addressed in particular the question of mercury and lead. One of his main objectives had been to determine if under the influence of KI, the lead was eliminated through the urine, the fecal matters, the blood, etc. His results had indicated clearly that blood did not contain lead. Melsens was willingly to admit Millon's result that blood contained silica and manganese but he wanted to know by what procedures Millon had assured himself that his glasses were totally resistant to the action of wet chlorine, of the HCl formed by the reaction between blood and chlorine, ammonia, acid phosphates, etc. Also, what precaution had been taken by Millon to assure himself that the manganese chloride formed during his process had not been carried into the samples he had analyzed, and thus altered his results. He could not understand the degree of accuracy reported by Millon, who had mixed 1 kg of serum with 3 kg of water (plus all the water used for washing in different stages of the analytical procedure) and had been able to detect 3 mg of copper and lead, a result beyond the known capacity of analytical chemistry (Melsens, 1848).

Melsens went on to describe the additional experiments he had conducted about the possibility that copper and lead were present in the blood of nine women, four men, one dog, and seven horses. He described in full detail all the precautions he had taken to ensure the absence of these two elements from all the vessels, water, filters, glasses, etc. used in his experiments: for example, he had put the blood inside capsules made of porcelain from Sèvres, previously washed with aqua regia and distilled water; he defibrillated the blood using a glass rod previously washed with aqua regia; the tube conducting the chlorine was made of white non-fusible glass; the chlorine, before bubbling into the blood, had been washed in a large flask containing water strongly acidulated with sulfuric acid; all his filters were previously washed with ammonia, aqua regia, and chlorinated water, etc. etc. None of his experiments showed the presence of copper or lead in the blood. To be double sure of his experimental procedure, he now took 1,600 g of horse blood and added to it the amounts of lead and copper believed to be present in normal human blood; he then repeated his operating procedure and had no difficult in recording the presence of the two elements (Melsens, 1848).

Melsens concluded his paper with some harsh comments about Millon's work: "…lead and copper existed only in the imagination of the learned professor from Val-de-Grace…It is to be hoped that even after Mr. Millon is called to give his opinion or advice on a medical-legal question he will be more careful than he has been in making these experiments in the presence of copper and lead in healthy blood" (Melsens, 1848).

Melsens's publication brought a strong reply from Millon; in his first note he repeated his claim that lead and copper were present in blood and remarked that those who had read his paper knew that it did not deserve such "gratuitous aggressions" (Millon, 1848b). In his second note he stated that in all his analyses he had employed vessels made of clay, porcelain, glass, etc., in which it was very easy to determine the presence of lead and copper. Nevertheless he admitted that soldiers used metal cooking materials, which could have affected his results (Millon, 1848c).

Proteinic materials

In 1851 Melsens published a short notice and a long memoir giving a historical review of the knowledge available about albuminoidal materials and the experiences he had carried on the modifications experimented by these materials in the presence of neutral salts and under the action of pure mechanical means (Melsens, 1851).

Melsens' results indicated that (a) changing the physical constitution of albuminous liquids by addition of soluble salts rendered the albumin precipitable by aqueous phosphoric acid and by acetic acid; the precipitate was redissolved by an excess of phosphoric acid but not by an excess of acetic acid; (b) the albumin of blood was different from that of the white of eggs; (c) when the white of eggs was shaken it transformed into an organized membrane totally different from fibrin; (d) the mechanical coagulation of albumin gave a true foam; serum blood foamed but did not yield an organized membrane; and (e) egg albumin was close to the state of fibrin in blood, which was not the case of serum albumin (Melsens, 1851).

Activated carbon

The possible catalytic explanation for the synthesis of sulfuryl chloride led Melsens to a more detailed study on the action of activated carbon (Melsens, 1873ef). He believed that it was reasonable to assume that contacting carbon with a solidifiable volatile liquid would result in the partial solidification of the liquid on the surface of the pores. Was this hypothesis valid for liquids, which had not been solidified even when cooled to very low temperatures? For example, to admit the solidification of chlorine, which had yet to be achieved, it was necessary to resort to the thermal phenomena accompanying this condensation, that is, to measure the amounts of heat released, as had been done with SO_2 (see above). When a gas became fixed on carbon, it would be necessary to overcome not only the heat of the attractions or cohesions of the possible three phases with carbon, but also to restore the heat loss of its condensation. These considerations led to ask in which direction the vapor pressure of the adsorbed liquid would change. To answer this question, Melsens used a Faraday tube (Faraday, 1823) (a glass tube shaped like and A, with one branch larger that the other) to study the adsorption of chlorine on carbon. He put charcoal in the long branch of the tube, saturated it with chlorine and then sealed the end. The long-branch was now heated in a water bath of boiling water while the short one was submerged into a freezing mixture. At a temperature above that of boiling chlorine, the chlorine disengaged from the carbon and returned to the gas state; eventually the internal pressure generated was enough to cause its liquefaction. Melsens remarked that in general, the equilibrium point would depend on the nature of the carbon, its quantity, the nature of the gas, etc. If the molecular attraction was strong enough, then all the liquid wetting the carbon had to experiment an increase in temperature. He observed that if the tube was taken out of the bath, the chlorine would began to boil spontaneously, condense again on the charcoal, while the short branch became covered with frost. These series of experiments could be reproduced as many times as desired, and thus performed at public lectures, allowing the audience to observed the various phases. Melsens extended them to the liquefaction of a large number of gases absorbed by charcoal when cold, and disengaged by a temperature not rising above 100°C: chlorine, ammonia, sulfur dioxide, hydrogen sulfide, hydrobromic acid, ethyl chloride, and cyanogen (Melsens, 1873ef).

Melsens remarked that very little information was available about the thermal phenomena accompanying these experiments. The most important one were the experiments carried on by Claude Pouillet (1790-1868) in 1822, based on the principle that the wetting of a solid by a liquid was accompanied by heat release (Pouillet, 1822). Pouillet measured the temperature elevation for 20 inorganic substances in a pulverulent state (e.g. glass, porcelain, brick, different metals and metallic oxides), and for 39 substances, which he named “organized” (e.g., charcoal, starch, plant roots, flours of different seeds, seeds, paper, thread, hair, wool, sponge, pork bladder, etc. etc.), when wetted by water, oil, alcohol, and ether; His results indicated that the temperature elevations for different solids were essentially the same with the same liquid, and for a given solid with different liquids, and that the elevation observed for organized substances was substantially larger than that for inorganic ones (Pouillet, 1822).

Melsens remarked that in spite of the careful experiments conducted by Pouillet his report did not contain information that allowed calculating the amount of heat released, or the ratio between the amount of the solid materials and liquids. For this reason, he was forced to conduct his own experiments in an apparatus of easy construction: A large glass case, surrounded by a hand towel, was positioned on a wooden support and filled with carded cotton. A thin glass tube, 15 cm long and 2 cm diameter, was put at the center of the cotton bed and partially filled with charcoal; the internal temperature changes were measured with a thermometer marked to the tenth of a degree. The desired amount of liquid being tested was introduced along the walls of the thermometer, down to the center of the charcoal bed. Melsens conducted a large number of experiments using water, alcohol, ether, carbon disulfide, and bromine, and registered the amount and the initial temperatures of the charcoal and the liquid, the temperature of the surroundings, and the temperature elevation after three minutes. The results, particularly with bromine, clearly justified Pouillet’s hypothesis that the wetting of a solid was accompanied by an increase in temperature. The results with bromine were particularly striking: with 1 part of carbon and 9 of bromine, the temperature elevation observed was higher than 30^0C, operating only with 5 to 10 g of carbon. Melsens believed that a higher temperature difference would be observed if the same experiment were conducted in an evacuated tube. He added that the volatile liquids (e.g. bromine, cyanhydric acid, carbon disulfide, ether, and alcohol) condensed in the pores of carbon could be only partially expelled by heating to 100^0C, at room pressure. He understood that the values of many physical properties were missing in order to justify the assumption that the liquids were partially solidified in the pores of carbon. Melsens also used the Faraday tube to determine the lower temperature at which the volatile liquids adsorbed by carbon would be released and condensed in the shorter arm (Melsens, 1873e).

Saponification of fats

On January 1855, Melsens was awarded a patent for a new process for the saponification of fatty materials, by which they were decomposed into fatty acids and glycerin, using only common or acidulated water, at a pressure slightly different from the pressure usually employed. The water was used alone or mixed with a few hundredths of sulfuric or other powerful acid, or saturated with boric or other weak acids. The process was carried at a temperature between 171^0 to 204^0C. The fatty materials were decomposed partially or totally, according to the conditions or duration of contact with the common or acidulated water. After separation, the fatty acids could be used for the manufacture of candles or soaps. Melsens' process allowed transforming in one step, tallow or other fatty bodies into fatty acids. The process was conducted in an arrangement of two boilers, one above the other, and connected by means of pipes, in which there were taps so as to allow communication to be made between the two boilers at certain stages of the process, and to allow the water and fatty materials to fall in showers upon the fatty body in the lower boiler (Melsens, 1855b).

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