

## EDME-JULES MAUMENÉ

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### ABSTRACT

Edme-Jules Maumené (1818-1898) was a French chemist who determined the atomic mass of a number of elements, studied in detail the physical and chemical properties of sugars, the manufacture of wine and alcoholic fermentation, the toxic effects of fluorides and zinc, and the properties of suint. He developed a new theory to explain chemical reactions, and a new chemical nomenclature (both failed).

**Keywords:** atomic mass, chemical reactions, fermentation, fluorides, sugars, suint, zinc.

### RESUMEN

Edme-Jules Maumené (1818-1898) fue un químico francés que determinó las masas atómicas de varios elementos, estudió en detalle las propiedades físicas y químicas de los azúcares, la fabricación del vino, los efectos perniciosos del zinc y los fluoruros, la fermentación alcohólica, la materia grasa de la lana de oveja, etc. Asimismo, desarrolló una nueva teoría de las reacciones químicas y una nueva nomenclatura química (ambas fallidas).

**Palabras claves:** azúcares; fermentación; fluoruros; masa atómica; reacciones químicas; suint; zinc.

## INTRODUCTION

### Life and career (Jacques, 1996)

Very little information is available about Edme-Jules Maumené. He was born in Paris on November 11, 1818; in 1846 he earned his doctorate in sciences from the Faculty of Sciences in Paris after successfully defending a thesis about the equivalents of chlorine, silver, and potassium (Maumené, 1846a). Afterwards he was appointed professor of chemistry and physics at École Municipale de Reims and at the Faculté Catholique of Lyon. He was member of the council of public health of the district of Reims and of many scientific societies. In 1851 the Académie des Sciences awarded him one-half of the Montyon Prize (section Statistics) for his paper on the analysis of the water of city of Reims (Maumené, 1850c). As customary for all candidates to the Académie des Sciences he published a booklet describing his research achievements (Maumené, 1884). He failed three times in his attempts, twice for a place in the Section of Rural Chemistry (1884 and 1896), and once for a place in the Section of Chemistry (1897). Maumené passed away in 1898.

### Scientific contribution

Maumené wrote about 140 papers and books (Maumené, 1853, 1858, 1861, 1866, 1874c, 1876-1878, 1880, 1893, 1894) about organic, mineral, and physical chemistry, and physiology. His most important contributions were in the chemical and physical properties of sugar, and in winery. In addition to the subjects described below, he also announced the discovery of a new copper oxide (Favre & Maumené, 1844); designed an improved alembic (distiller) (Maumené, 1847) and a new gas hydrometer; (Maumené, 1874b); experimented on complementary colors (Maumené, 1850a); studied the analysis of fatty oils by means of sulfuric acid (Maumené, 1852); the action of fluorides on animals (Maumené, 1854c); the alcoholic fermentation (Maumené, 1857); the distillation of liquid mixtures (Maumené, 1863b); the action of oxygen on wine (Maumené, 1863c); proved that sodium arsenate did not transform into pyroarsenate or metarsenate (Maumené, 1864a); etc.

### Atomic masses

#### Silver, chlorine, and potassium

Maumené wrote that after Jean-Baptiste André Dumas (1800-1884) had reported the results of his experiences on the composition of water and CO<sub>2</sub> (Dumas, 1842) he had called on chemists to test William Prout's (1785-1850) hypothesis that the value of the atomic mass of an element was an integer multiple that of hydrogen (Prout, 1815; Maumené, 1846a). The experimental results on the subject suggested that the hypothesis was a good approximation for many elements but failed completely for substances like chlorine, potassium and silver. Of these three simple bodies, chlorine was the most important because an accurate determination of its atomic mass allowed easily determining the mass of most other metals. Presently, the atomic mass of chlorine was assumed to be 442.65, a value that deviated clearly from Prout's hypothesis, which required it to be 437.5 or 450 (on the basis C = 12.5). Jean Charles de Marignac (1817-1894) had recently reported that the calcination of 100 parts of potassium chlorate left 60.098 parts of potassium chloride and 100 parts of potassium chloride precipitated 192.269 parts of silver nitrate. These results indicated that the value of the equivalents of silver, potassium, and chlorine were 1349.01, 488.94 and

443.20 respectively (on the basis that C = 12.5) and 107.920, 39.115, and 35.456 respectively (on the basis H = 1) (Marignac, 1843).

Maumené believed that these results were not supported by indisputable facts and for this reason he decided to conduct his own experiments, based on the decomposition of silver chloride by hydrogen and the analysis of silver oxalate (Maumené, 1846a). The reduction with hydrogen could be done with great accuracy, taking very simple precautions. The silver chloride by prepared by reacting a boiling solution of very pure silver nitrate with HCl, in relative darkness, separating the white precipitate of silver chloride, followed by drying and melting in a porcelain crucible. The hydrogen gas was prepared by reacting zinc with aqueous sulfuric acid followed by washing and drying by means of concentrated KOH and sulfuric acid. The silver chloride was put in platinum boat located within a tube made of hard glass and heated under a stream of hydrogen, for 12 to 18 hours. The result of numerous experiments indicated that 100 parts of silver combined with 32.736 of chlorine. The ratio 32.736: 100 = 450: x indicated that the equivalent of silver was 1374.6, (with 450 as the equivalent of chlorine), or 109.97 with H = 1 (Maumené, 1846a).

Silver oxalate decomposed very easily under heating, particularly when done very slowly and mixed with sand to avoid explosions. Maumené reported that the procedure was extreme simple and accurate, but the results were plagued by problems encountered during the preparation of the silver oxalate. This salt was prepared by reacting silver nitrate with pure oxalic acid. In every case the reaction was accompanied by the formation of a small quantity of red vapors, originating from small of amount of residual silver nitrate present in the oxalate. Maumené also prepared silver oxalate by reacting silver nitrate with ammonium oxalate. Interesting enough all the above experiments led to the same value of the equivalent of silver, 1350.3225. This figure became 442.04 when referred to the reduction of silver chloride, as follows: 100 (Ag): 32736 (Cl) + 1350.3225: x = 440.04, as the value of the equivalent of chlorine. The value of the equivalent of potassium was calculated in the same manner: 487.78. These three values of the equivalent compared very well with the results obtained by Jöns Jacob Berzelius (1779-1848) and Marignac:

	<u>Marignac*</u>	<u>Maumené</u>
Chlorine	443.38	442.04
Silver	1319.66	1350.32
Potassium	488.86	487.78

\*(1843)

Maumené explained the small difference by the fact that the glass vessel where all the chemical reactions were carried, experimented a small increase in weight caused by the cinders of the stove (Maumené, 1846a).

As mentioned above, this work was the subject of the doctoral thesis of Maumené.

## Iron

In 1846 Maumené was charged with analyzing the wires offered for the telegraph of the railway Du Nord; during his experiments he noted that the iron was extremely pure and used this fact to determine a better value of its equivalent, which at that time was reported to vary between 339.23 to 350 (Maumené, 1850c). Maumené dissolved the metal in weak aqua regia and precipitated the oxide by means of ammonia. The filtrated solid was carefully washed with hot water to eliminate the ammonium

chloride, dried in a stove at 110 °C, and then calcined in a platinum crucible. The average result of 6 experiments yielded the value of 35.01 for the equivalent. The corresponding value of (one-half) the atomic mass was 28.00 (the accepted value of the atomic mass of iron is 55.847).

### Reciprocal action between metals and concentrated sulfuric acid

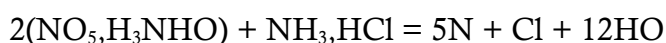
Maumené wrote that the reaction between concentrated sulfuric acid and metals had been studied profusely and the conclusions obtained assumed to be absolute (Maumené, 1846b). For example, it was accepted that warm sulfuric acid in contact with a metal (M) released SO<sub>2</sub>, and the oxide of the metal, and transformed them into their pure sulfates. This reaction was represented by the equation  $M + 2SO_3 = MOSO_3 + SO_2$ . According to Maumené, however, the facts were not always as simple as the theory, and in some cases their complication was truly surprising. For example, heating copper with sulfuric acid produced the expected SO<sub>2</sub> and cupric sulfate, but also a black powder perfectly similar with cupric oxide, although some chemists, such as Jean-Pierre Barruel (1780-1838) considered it to be cupric sulfide (Maumené, 1846b).

Maumené mentioned that during the preparation of large quantities of SO<sub>2</sub> by means of copper he had observed the appearance of this sulfide and noticed that tins formation was not the result of a simple action. The decomposition of the acid was accompanied by the deposition of a *brown* powder, very sensitive to the action of air, which chemical analysis indicated that it was cuprous sulfide, Cu<sub>2</sub>S. Its color began immediately to become darker and eventually to turn black. The sulfide, after its formation, promptly combined with some cupric oxide to form a compound Cu<sub>5</sub>S<sub>2</sub>O = 2Cu<sub>2</sub>S,CuO, which then lost 2 equivalents copper to become Cu<sub>3</sub>S<sub>2</sub>O = 2CuS,CuO; and finally with some additional cupric oxide, to yield a final product composed of equal amounts of cupric sulfide and cupric oxide: 2CuS,CuO + CuO = 2(CuS,CuO). According to Maumené, the amounts of sulfide and oxisulfide formed were were not very large extent: The quantity of copper, which passed into the state of sulfate, was about 50 times that of the copper contained in the oxisulfide (Maumené, 1846b).

Further experiments with other metals (lead, bismuth, tin, antimony, and arsenic) showed that this behavior was not restricted to copper alone: the lead sulfate deposited was always strongly colored gray by the sulfide. Bismuth, tin, antimony and arsenic did not show the presence of sulfide, but towards the end of the reaction a small quantity of sulfur was always found to condense on the cold parts of the vessel. Maumené believed that the formation of sulfide and oxisulfide was a result of the great affinity of sulfur for the metals; at the beginning of the reaction, a small quantity of the sulfuric acid was decomposed by the metal, which deprived it of its oxygen and its sulfur at the same time (Maumené, 1846b).

### Preparation of nitrogen and chlorine

According to Maumené, many methods were available for preparing nitrogen, but independently of the separation of the components of air by means of metals, all the rest were complicated and inconvenient. He now reported about a process he had developed, which also produced chlorine (Maumené, 1851). The new process was based on the reaction between ammonium nitrate and ammonia chloride at high temperature, as described by the following reaction:



As soon as the temperature of the mixture reached the fusing point of the nitrate, a very strong action took place, producing the results indicated. After the first few moments the heating body should be withdrawn, and the reaction left to proceed by its own means. Maumené warned that the process was dangerous because it gave only gaseous products, very rapidly, and in large quantity, causing a risk of explosion. In addition, the reaction mixture assumed a pasty state and swelled considerably, sometimes choking the neck of the retort. He suggested that in order to make it safe a small amount of materials be operated on at a time, and they should be previously mixed with about four times their weight of sand. In this manner, the gases are given off quietly, the heat released is controlled, and the reaction proceeds quietly. He recommended reacting 75 g of dry ammonium nitrate with 25 g of dry ammonium chloride, mixed with 400 g of sand. This mixture yielded 26 L of nitrogen and 5 of chlorine. Using very pure reagents in these proportions the only products are nitrogen and chlorine with no production of nitrogen chloride. Since his process did not use manganese dioxide and other materials, which were daily increasing in price, may perhaps prove of much value to the chemical industry (Maumené, 1851).

### Zinc poisoning

In 1850 the physician Charles Flandin (1803-1887) published a paper claiming that zinc compounds were innocuous to human health (Flandin, 1850). This note brought a reply from the physician Hector Landouzy (1812-1864) and Maumené, calling the attention respect the potential health dangers involved in the managing of *galvanized zinc* wire (Landouzy & Maumené, 1850). They wrote that the iron wire employed for securing the corks of champagne, was sent in bundles of 1 to 10 kg to workmen called *tordeurs* (wire twisters), which expertly cut and twisted from ten to twenty threads of wire at a time. The workmen had carried this operation for many years, under very bad hygienic circumstances as regards ventilation, but never experienced any bad effects from it until the beginning of January 1850, when a galvanized wire substituted the common iron wire. Soon after, the workmen began to complain of the taste as of a sweetish powder in the throat, an incessant tendency to cough and spit, shivering, and general malaise. Several of them were affected with symptoms, which were attributed to zinc: sore throat, swelling and ulceration of the tonsils, inflammation of the palate, white pellicles on the gums, salivation, fetid breath, colic, and diarrhea. Inspection of the works showed that the galvanized wires with which they worked had been made hastily and carelessly, and were covered with a dusty powder, which escaped abundantly during the twisting, and especially the beating of the wires. Inspection of the powder indicated that it consisted of zinc, zinc carbonate and oxide, an alloy of zinc and iron, and iron oxide. It contained no trace of lead. Elimination of the dust resulted in disappearance of the symptoms and effects and return to normality. Landouzy and Maumené suggested that the health authorities take the proper action to eliminate this source of poisoning (Landouzy & Maumené, 1850).

### Sugars

Maumené carried on a detailed study of the physical and chemical properties of sugars (Maumené, 1850b, 1854ab, 1856, 1863a, 1869, 1870, 1871a, 1872, 1874a, 1875, 1876ab, 1878, 1881) In his first paper he announced the discovery of a new and powerful analytical method for detecting the presence of small amounts of sugars in fluids by means of tin dichloride (Maumené, 1850b). He wrote that chemists had

developed many procedures for detecting the presence of sugar, even in the case of diabetes; Unfortunately, none of these methods was simple enough to be applied in medical practice. Dr. Landouzy had asked him about the possibility of developing a reactive paper, capable of detecting sugar in urine (Maumené, 1850b). The action of chlorine upon sugar was imperfectly known and the experiences carried by Maumené on the subject allowed him to identify many inaccuracies claimed by even famous chemists. For example, Justus von Liebig claimed that chlorine, even dry, reacted with cane sugar when heated to about 100 °C, while at room temperature the reaction was extremely slow. In every case a brown substance, partly soluble in water, was formed, which turned brilliant black when dried. Chlorides and perchlorides acted in the same manner. All sugars, and similar bodies, for example, lignin, cotton, paper, starch potato flour, linen, and hemp, behaved in the manner as cane sugar, they all experimented the dehydration that led to the formation of brown-black substance. Maumené experiments showed a different result: dry chlorine did act upon dry sugar, although at room temperature the action was slower but eventually resulted in the formation of the black substance. This common result suggested him of the possibility of reacting the sugar-containing fluid with a chlorine derivative and detecting the black color with a paper or tissue. For this purpose, he selected tin dichloride (Maumené did not explain why he chose this salt, in particular!). A piece of paper or tissue, which had previously been impregnated with a solution of tin chloride and then dried, was introduced into the fluid being tested, and then heated to 130°-150 °C (to accelerate the reaction) for a few minutes. If sugars were present, the tissue would become brown black, more or less intense. Maumené found that a piece of tissue made of merino wool was the best tissue for his test. It was prepared by immersing a 2x7 cm piece of merino wool tissue in an aqueous solution of commercial  $\text{SnCl}_2 \cdot 5\text{H}_2\text{O}$ , containing 100 g of salt per 200 g of common water, and then dried over a water bath. A drop of the fluid being tested was put on the cloth and the wet cloth dried over a flame of alcohol during a minute. Maumené wrote that his test was extremely sensitive; 10 drops of diabetic urine diluted in 100 cm<sup>3</sup> yielded a liquid that darkened promptly the merino tissue; ordinary urine, urea, and uric acid did not react with the cloth. The procedure did not allow a quantitative determination of the amount of sugar present, and did not differentiate between sugars of different nature, Maumené found that mercuric chloride and antimony chloride acted in the same manner as tin dichloride as the reagent. Maumené added that his reagent could be used for detecting sugar in wines and for dyeing wool brown or solitaire; the color could be obtainable at a low price, and be very fast (Maumené, 1850b).

In a following paper Maumené wrote that he has now been able to use his procedure to determine the *amount* of sugar present in a fluid. He found that the action of action of tin dichloride upon sugar could be regulated by using a large excess of the reagent, for example, 15 to 30 g of chloride to 1 of sugar, The final mixture was black, but instead of being formed of two parts, one soluble and the other insoluble (partial reaction), this time it was composed of a single product, completely insoluble in water (total reaction). Elemental analysis of the product indicated that its composition corresponded to the formula  $\text{C}_{12}\text{H}_4\text{O}_4$  (on the basis C = 12.5), that is, cane sugar less seven equivalents of water:  $\text{C}_{12}\text{H}_{11}\text{O}_{11} - 7\text{HO} = \text{C}_{12}\text{H}_4\text{O}_4$ . The same result was obtained with grape sugar (dextrose), cellulose, dextrin, etc., that is, with all the compounds of formula  $\text{C}_a(\text{HO})_b$ . In other words, the action of the dichloride was a simple struggle competition between the sugar and the other analog substances to keep their hydration water. For this

reasons Maumené suggested naming *caramelin* the final black substance ( $C_{12}H_4O_4$ ) (Maumené, 1854a).

The quantitative procedure was based on the hypothesis that the liquid contained only one kind of sugar and no other matter of the formula  $C_a(HO)_b$ . The quantity of sugar present was first determined approximately by means of addition of a few grams of tin dichloride. The solution was then evaporated to dryness and the residue heated for about 10 minutes to  $120^{\circ} - 130^{\circ} C$ , to change the sugar to caramelin. The residue was again treated with water to verify if the action of the chloride had been complete or no. In the last case the resulting solution would be colored brown. The procedure was repeated until the new solution was colorless, meaning that the sugar had been totally converted into caramelin (insoluble in water). The final residue was now treated with a weak solution of HCl or sulfuric acid to remove all the impurities present in caramelin. It was then dried and weighed (*P*). The proportion of sugar was determined using the fact that  $C_{12}H_{11}O_{11} = 2187.5$ ,  $C_{12}H_4O_4 = 135.0$ ,  $C_{12}H_{12}O_{12} = 2300$  (grape sugar),  $C_{12}H_{10}O_{10} = 2025$  (dextrin), and  $C_{12}H_4O_4: C_{12}H_{11}O_{11} = P: x$  (the second term was replaced by 2300 or 2025 if the sugar was grape sugar or dextrin) (Maumené, 1854a).

Maumené indicated that the purpose of the first step was to determine exactly the proportion of sugar. The same volume of liquid was taken again and mixed with 15 or 16 g of tin dichloride per gram of sugar. The full procedure described above was repeated. The *caramelin* thus obtained was pure and finely divided. Its weight gave exactly the quantity of sugar. Once again Maumené regretted that his procedure did not allow the separation of the various kinds of sugar, and when the sample contained simultaneously grape sugar and cane sugar (Maumené, 1854a).

Maumené remarked that diluted acids converted cane sugar into non-crystallizable inverted sugar (so called from its action on polarized light). It was generally accepted that only acids could effect this transformation and that the rate of the reaction increased rapidly with temperature. The change involved the combination of the sugar with one equivalent of water, but no one had sufficiently investigated the part played by water alone. He now wanted to report his work on the question and announce, "that perfectly pure water sufficed for effecting the important modification in question" (Maumené, 1854b). According to his experiments, the purest sugar candy in solution in pure water gradually changed, even without heat, into non-crystallizable sugar. He wrote that the reaction was easily followed with the use of a sacharimeter: the dextro rotating power was seen to decrease constantly and was particularly large when employing sugar candy. The intensity of the decrease varied with sugar samples of different types (for example, candy and loaf sugar) and years. Higher temperatures clearly favored the reaction. Under the same conditions glucose and gum suffered no alteration.

The results of Maumené's experiments allowed understanding the alterations that happened in sugar beet *before* extraction of the sugar: (1) the roots gave a product diminishing in quantity during the season, even with the entire roots, since the water had remained longer in contact, and (2) the desiccation processes based on heat had the inconvenience of determining a primary alteration of the sugar, without preventing that which would occur at the time of extraction. Maumené also found that organic acids did not sensibly increase the action of water and that the effect of water on cane sugar should be taken in consideration when analyzing sugar and gum syrups (Maumené, 1854b).

In 1856 Maumené reported a new process for extracting sugar from all kinds of vegetables (Maumené, 1856). He wrote that all the known processes for extracting

sugar from vegetables were highly inefficient, they yielded about 50% of the sugar contained in beet sugar and a little more than 33% that in cane sugar, even in the best conditions. He believed that their main fault layed in the mode of treatment. Sugar exposed to the action of cold water underwent a known change (see above), which prevented its crystallization. On cropping, the beetroot was deprived of soil, leaves, and upper section, and stowed away until processing. In such a state it ceased to live and become a *flask of sweet water*; the longer this process, the larger the amount of sugar which became inverted. Obviously, this problem originated from the fact that sugar manufacturers kept their stock of beets for a long time before they subjected to process. Several chemists had shown that the mobility of the element of the sugar (responsible for its inversion) disappeared instantly when the sugar was treated with enough lime to form a saccharate. The work of Auguste-Pierre Dubrunfaut (1779-1845) was quite conclusive on the subject: he had prepared the calcium saccharate and found that after 25 years its sugar had remained unchanged (Dubrunfaut, 1851). This finding suggested that the best method for avoiding the loss of more than 50% of the available beet sugar, or 33% of cane sugar, was to crush out the juice at once, as fast as the roots were dug up, discharged it into cisterns, and throw in enough lime to transform the sugar into calcium saccharate, which would keep the crystallizable sugar intact for one year. The manufacturer could recover this sugar by the simple addition of CO<sub>2</sub> or other substances of similar action (Maumené, 1856).

Maumené ended his paper with a discussion of the industrial and economic consequences of the production process he recommended (Maumené, 1856).

In a footnote to this paper, the editors of the journal remarked that they had published this paper for the interesting observations reported by Maumené, but they abstained of passing judgment on the industrial importance of the same.

According to Maumené, non-sugar diabetes presented an interesting characteristic that had not been reported anywhere. The weight of diabetic urine left after evaporation at 100 °C was extremely small, about 2.7 to 2.8 g/L at the most. Since the daily discharge of urine was no more than 8 L/day the total amount of solid matter did not exceed 22 g/day (Maumené, 1863a). This extract was dark brown, smelling strongly like urine, with the particular intensity of all diabetic urines, and full of crystals. Maumené dissolved the residue in water, added a slight excess of lead acetate, precipitated the excess of the latter with hydrogen sulfide and ammonia, and separated the solid by filtration. The new filtrate was now yellow and could be decolorized with carbon black at boiling conditions. The filtrate was evaporated on a water bath to a syrupy state and then to crystals. The crystals, washed with alcohol and dried over a paper, were now white. Analysis of the same indicated that they contained by weight, 53.33% sodium chloride, 38.75% urea, and 7.91% of other salts; no sugar was present (Maumené, 1863a).

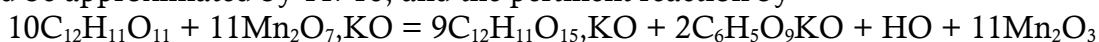
Maumené published several papers on the nature of inverted sugar (Maumené, 1869, 1875, 1876a) and which led to a lengthy discussion with Dubrunfaut. Dubrunfaut believed that inverted sugar was a mixture of glucose and levulose in a one-to-one molar ratio, and that the levorotatory action of inverted sugar was the result of a molecule of cane sugar splitting into one of glucose and another of levulose. Maumené disagreed with these views. He prepared pure inverted sugar by treating sugar candy with fuming HCl in a water bath for 3 to 4 hours, until he saw the beginning of a coloration process. The inversion was total, as indicated by the saccharimeter. The excess HCl was eliminated with silver chloride and the excess silver chloride with hydrogen sulfide. Pure inverted sugar had the full appearance of yellow honey or of



grape sugar obtained by evaporation of purified grape juice. It was neutral, had a very pleasant taste, and was soluble without leaving a residue. Maumené tried to separate the two sugars by means of sodium chloride. For this purpose, he evaporated a solution containing a solution of inverted sugar and salt and obtained a mixture of beautiful crystals of a well-defined compound of dextro glucose and sodium chloride, and non-crystallizable mother liquor composed only of levulose. Analysis of the mixture indicated that it contained approximately 12% glucose and 88% of levulose, a composition quite different from that reported by Dubrunfaut (Maumené, 1869).

In another paper, Maumené described the results of a series of new experiments on the preparation of inverted sugar, which resulted in more complicated view of the results: appearance of a third component, neutral sugar with no optical activity (Maumené, 1875). He wrote that cane sugar consisted of  $C_{12}H_{22}O_{11}$ , was crystallizable, and deviated polarized light to the right. Inverted sugar was composed of  $C_6H_{12}O_6$ , was not crystallizable, and gave a left-handed rotation. Maumené new results indicated that inverted sugar had no constant composition, but was a mixture of various proportions of glucose, chylarose (name given by Maumené to levulose), and neutral sugar. Using a given amount of candy sugar was practically impossible to obtain constant amounts of glucose and chylarose or a constant rotatory power. The composition varied with the temperature, length of the reaction, acid employed, proportion of the reactants, etc. He succeeded obtaining an optically neutral sugar by the following procedure: He heated a mixture of white Narbonne (a commune in Southern France) honey and alcohol of  $90^\circ$ , and then let the mixture cool to near  $0^\circ C$ . The heavy layer was separated and treated with water to give a fluid, which was easy to examine with a saccharimeter. The zero-reading indicated that it contained neutral sugar. Upon heating, this product could give a sensible rotatory power. The same result was obtained by treatment with limewater and  $CO_2$ . Maumené added that inverted sugar burnt much more readily than common sugar, a fact of importance in analysis when the quantity of ash was to be ascertained (Maumené, 1875).

Maumené also studied the oxidation of sugar by means of potassium permanganate (Maumené, 1872). In his opinion the information available was very confusing, probably a result of the optical activity of sugar. Maumené's experiments indicated that potassium permanganate oxidized sugar producing two new acids, which he named *hexepic acid*,  $C_{12}H_{12}O_{16}$ , and *trigenic acid*,  $C_6H_6O_{10}$ . He believed that the discovery and preparation of these acids were clearly indicated by his theory about the exercise of affinity, assuming the values 171 and 158 for the equivalents of cane sugar and potassium permanganate, respectively (Maumené, 1872). The two reagents were very soluble in water and could be mixed at a low temperature. The ratio 171/158 was 1.08, representing the number of permanganate acting upon one atom of sugar. This result could be approximated by 11/10, and the pertinent reaction by



The above reaction showed that both acids were generated *simultaneously* and by the same reaction. Maumené mixed 200 g of sugar-candy dissolved in 2 L of water with the same weight of permanganate dissolved in 4 L of water, while keeping the sugar solution in rapid agitation during the mixing process. As a result, the temperature rose to  $45-48^\circ C$  while the manganese turned to a black solid clot of  $Mn_2O_3$ . The colorless filtrate was perfectly neutral, no longer tasting of sugar, and having a rotatory power similar and nearly equal to that of the sugar (value and direction). The filtrate gave a white crystalline precipitate with lead acetate, which on treatment with hydrogen

sulfide, filtration, and evaporation at a gentle heat, yielded the hexepic acid. After removal of the lead precipitate, the filtrate gave a second white precipitate with tribasic lead acetate, and this by a similar treatment to that just described, gives the second acid. Maumené also reported the preparation and properties of several salts of the new acids (Maumené, 1872).

In 1878 Maumené announced the discovery a third acid (*diehic acid*,  $C_4H_4O_8$ ) resulting from the oxidation of sugar by potassium permanganate (Maumené, 1878).

In 1871 Maumené reported that he had been able to prepare a saccharate of ordinary sugar and sodium chloride in large and distinct crystals (Maumené, 1871a). The crystals were sometimes a centimeter long, quite transparent and colorless, had the form of orthorhombic prisms of about  $136^\circ$ , and contained 14.65 parts of salt per 100 of sugar. The sugar contained in this body was found to possess the same rotatory power as normal sugar and not to react with the cupro-potassium liquor. This saccharate was prepared by dissolving 85 parts of highly pure sugar and 15 of sodium chloride in cold or slightly warm water, followed by evaporation with dry air in a glass bell containing a reservoir of sulfuric acid (Maumené, 1871a). In the same year he reported the synthesis of the saccharate of sodium iodide of formula  $(C_{12}H_{11}O_{11})_4.(NaI)_4(HO)_4$ , which he proposed be employed as sweet iodide. This compound crystallized in very large crystals of relative density 1.854. Once again, the rotatory power of sugar remained unaltered (Maumené, 1871b, 1876-1878).

### *Organic analysis*

Maumené wrote that the common methods of chemical analysis of organic substances had the limitation of reporting the oxygen content by difference and not directly (Maumené, 1862). Edouard Henri Baumhauer (1820-1885) had tried to solve this problem by a very complicated and not recommendable procedure (Baumhauer, 1855). Maumené proposed that instead of burning the tested substance with cupric oxide, it should be oxidized with a mixture of 75% lead monoxide (litharge) and 25% of calcium phosphate (to prevent melting). The resulting substances were water,  $CO_2$ , and a residue of lead, which could be weighted exactly. Complete removal of the phosphated litharge was achieved by putting it in a crucible mixed with twice its weight of pure litharge. This procedure provides a fourth relation, which allowed determining the oxygen by *analysis* and not by difference, using the following relation:

$$\text{oxygen} = \frac{8}{9}(\text{water}) + \frac{8}{11}(\text{CO}_2) - \frac{8}{103.5}(\text{lead})$$

Where carbon =  $(3/11)(CO_2)$ , hydrogen =  $(1/9)(\text{water})$ , and (weight of) substance = carbon + hydrogen + oxygen.

If the substance also contained nitrogen, then (weight of) substance = carbon + hydrogen + oxygen + nitrogen. The nitrogen could also be determined by the usual

procedures, with the relation  $\text{nitrogen} = \frac{14}{17}(\text{ammonia})$  (Maumené, 1862).

### *Isomorphism - non-existence of pyro and metaarseniates*

Maumené wrote that Eilbert Mitscherlich (1794-1863) had stated originally that when acids and bases were combined in the same degree of saturation, they not only showed the same crystalline form but also possessed the same chemical properties; in other words, they were *isomorphic* (Mitscherlich, 1820). Afterwards he had added that "every

arsenate had a corresponding phosphate, composed of the same proportions, combined with the same number of atoms of water of crystallization, and possessing, at the same time, the same physical properties (Mitscherlich, 1821); in other words, the only difference between the two series was that the radical of the acid of one series was phosphorus, and arsenic of the other. These statements were believed to be natural laws and, consequently, had led so chemists to believe that arsenates underwent, when heated, the same changes as the phosphates" (Maumené, 1864a).

Maumené believed that the last statement was wrong: sodium arsenate never gave pyroarsenate or metaarsenate. His experiments indicated that sodium arsenate submitted to an intense heat, suddenly or controlled, or prolonged for some hours, it did not undergo the slightest change of the sort. Not only that, dissolved in water, and then mixed with a solution of silver nitrate, it always gave a brick-red precipitate of  $\text{AsO}_5 \cdot 3\text{AgO}$ .

### *Suint*

Louis Nicolas Vauquelin (1763-1829) was the first to make a detailed qualitative study of suint (sheep wool grease), which at that time was thought to be a unique material of fatty nature (Vauquelin, 1804). He described it as oil combined with KOH and forming a true soap with potassium carbonate, because with acids it effervesced. It also contained a little of animal material, potassium acetate, calcium hydroxide, and potassium chloride. He also believed that it contained a sulfur compound because it produced a precipitate with barium chloride. Years afterwards, Michel Eugène Chevreul (1786-1889) reported that the wool of merino contained 31.23% pure wool (after extraction with alcohol), 32.74% of suint soluble in water, 8.57% of suint insoluble in water and composed of olein and stearin, and 27.24% of soil (Chevreul, 1829). As seen, the fraction soluble in water continued to be unimportant and assumed to be soap mixed with salts. Long afterwards, Chevreul published a second paper where he now identified 29 different substances present in suint, among them copper (Chevreul, 1857).

This lack of information led Maumené and V. Rogelet to carry additional experiences on the soluble part of suint and conclude as follows: (1) the soluble part of suint was a mixture of salts, mainly organic with potassium, and a small amount of calcium and magnesium; no sodium was present; (2) the suint was neutral; (3) upon calcination, the mixture of potassium salts left a residue of potassium carbonate, exempt of sodium and mixed only with potassium chloride, potassium sulfate, potassium silico-aluminate, potassium phosphate, a little of calcium carbonate, magnesia and the oxides of iron and manganese; (4) 100 kg of wool (without soil) contained 46 kg of pure wool, 10 of olein and stearin, 22 of dry suintate, and 22 of water; and (5) 100 parts of the saline portion contained 86.78 kg of potassium carbonate, 6.18 of potassium chloride, 2.83 of potassium sulfate, and 4.21 of salts of silico-aluminate, phosphates, and the oxides calcium, magnesium, potassium, iron, manganese, and copper (Maumené & Rogelet, 1865).

Maumené and Rogelet made the curious comment that in France lived about 50 millions of moutons, which in case of war could be washed to yield 28,100 ton of saltpeter (to manufacture gunpowder) (Maumené & Rogelet, 1865)!

### *Fusibility of salts*

Maumené wrote that Alexander Étard (1852-1910) had recommended replacing oils baths by a melted equimolar mixture of the nitrates of potassium and sodium and that

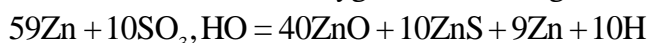
accidentally he had been led to study the fusibility curves of various mixtures of salts, in particular, those of binary and ternary nitrates (Maumené, 1883). All the nitrates studied were carefully purified before used. The melting points of purified potassium nitrate, sodium nitrate, and their equimolar mixture, were 327°, 298°, and 218 °C. Maumené also reported the melting temperatures of mixtures containing 1, 2, and 3 equivalents of these two salts.

### *General Theory of the Action of Affinity*

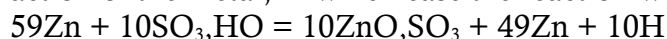
Between 1864 and 1844 Maumené published 47 papers describing what he believed was a completely new approach for explaining the correct course of a chemical reaction, without the need of assuming the theories of types and substitution. In his first paper (Maumené, 1864b) he described the basic principle of his new theory of the action of chemical affinity. According to him, chemical action was executed by contact, that is, it took place only at an infinitely small distance. Considering, for example, the interaction between a metal M and sulfuric acid, SO<sub>3</sub>,HO, it could only occur between molecules of the two bodies located at an infinitesimal distance of the surface of their separation. In addition, it had to satisfy to rule that all every action is equal to the reaction, that is, the action of the metal upon sulfuric acid had to be identical with the action of the acid upon de metal. The infinitesimal distance over which extended the action of the metal upon those of the acid had to be identical to the infinitesimal distance over which extended the action of the acid molecules upon those of the metal. Consequently, this distance  $\alpha$  had to be equal on both sides of the surface that separated the molecules capable of reacting. Thus, it was not the total mass of both bodies stored in a flask that exerted immediately this action; it was only that between two layers infinitively thin and of identical thickness: The mass of these two layers was proportional to their density; if we called M and M' the masses of the weights having density D and D' we had M: M' = D: D'. Assuming now the action of zinc on sulfuric acid and taking M to be zinc, then M = the equivalent of zinc = 32.5 and D = 7.2. For sulfuric acid, M' would the unknown and D' = 1.85. Hence the relation 7.2:1.85 = 32.5:M' and M' = 8.35. This number would be a fraction of 49, the equivalent of sulfuric acid, this, 49/8.35 = 5.87. In other words, independently of how much zinc was in contact with sulfuric acid, the *real* direct action of the metal upon the acid took place between 1 equivalent of metal and 1/5.87 equivalents of acid, or what was the same, between 59 molecules of metal and 10 of acid: 59Zn + 10SO<sub>3</sub>,HO. How was the action realized in practice? If the zinc acted more strongly on the sulfur than on the oxygen, we would have:



If the action of Zn on oxygen were stronger than on sulfur we would have



Both actions implied the formation of ZnS, which was known not to occur in practice. Hence, we had to assume that the acid SO<sub>3</sub> was very stable and resisted the action of the metal, in which case the reaction would have to be



Maumené went on to analyze other possibilities including the above reaction carried with dilute acid, at lower and higher temperatures, other acids, other reactions, etc. (see above). In total, he published 47 papers trying to justify how his theory explained the experimental results of the different reactions analyzed (Maumené, 1864b).

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