

## RESEÑA

## Félix-Polydore Boullay

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**RESUMEN.** Félix-Polydore Boullay (1806-1835), un químico Francés, murió a los 29 años de las heridas sufridas durante una inflamación de éter. A pesar de su joven edad, alcanzó a hacer importantes contribuciones a la teoría de la eterificación (bajo la guía de Dumas), a la química de los haluros dobles, el volumen de los átomos, de los ácidos úlmico y azulmíco.

**ABSTRACT.** Félix-Polydore Boullay (1806-1835), a French chemist, died at the age of 29 from the wounds he suffered from burning ether. In spite of his young age, he made significant contributions to the theory of etherification (under the guidance of Dumas), to the chemistry of double halides, the volume of atoms, ulminic acid, and azulmic acid.

## LIFE AND CAREER

Very little information is available regarding the life of Félix-Polydore Boullay; most of what is known appeared in the obituaries published by Félix Boudet and Jean Baptiste Alphonse Chevallier (1793-1879).<sup>1,2</sup>

Félix-Polydore Boullay was born in Paris in March 16, 1806, the son of Pierre François Guillaume Boullay (1777-1869), a pharmacist, at one time President of the *Académie Nationale de Médecine*. He received his basic education at the famous school, *l'Institution Massin*, where he was very successful, finishing his studies within 10 years. At the age of 18 he took the courses on physics and mathematics given by Jacques Babinet (1794-1872) at the *Lycée Saint-Louis*, and on August 5, 1825, received the degree of *bachelier ès-lettres*. He then went to study chemistry with Antoine Bussy (1794-1882), professor at the *l'École de Pharmacie*, and became familiar with chemical manipulations in the laboratory of the *École* and at the *Athénée*, under the guidance of Jean-Baptiste André Dumas (1800-1884). Afterwards he was appointed préparateur to Dumas's class and followed him to his laboratory at the *École Polytechnique*. In addition, he devoted himself to the study of pharmaceutical manipulations, at home and under the guide of his father. In 1827 he read to the *Académie des Sciences* a memoir on double iodides,<sup>3</sup> which was considered of enough quality to be published in the *Recueil des Savants Étrangers* [1].

On April 11, 1828 Boullay received his degree as *bachelière ès-sciences*, in 1829 his *licencié ès-sciences*, and on February 20, 1830, he defended at the *Faculté des Sciences de Paris* his thesis on the volume of atoms

and the modifications that they experiment in chemical combinations.<sup>4</sup> On March 1830, he was granted the degree of *docteur ès-sciences* after presenting a thesis on the ulmic and azulmic acids.<sup>5</sup> On March 4, 1834, the *École de Pharmacie* de Paris, awarded him his diploma of pharmacist, after passing all the required exams and defending with distinction his thesis on the successive modifications introduced on pharmaceutical formulations and practices.<sup>6,7</sup>

Boullay published, alone or in collaboration with Dumas or his father, several memoirs on double halides,<sup>3,8</sup> on the formation of diethyl ether and esters,<sup>9,10</sup> on the volume of atoms,<sup>4</sup> on ulmine (a brown amorphous substance found in decaying vegetation) and azulmic acid,<sup>5</sup> a note on the solubility of lead iodide,<sup>11</sup> and on pharmaceutical subjects.<sup>12-14</sup>

Polydore Boullay died on May 23, at the age of 29 years, after having suffered for four and a half years the consequences of a dreadful accident, which occurred in the middle of his work related to chemical manipulations. Burns caused by liquids were very common during the 19th century and were usually caused by negligence or distraction of the operator. The most common were due to inflammation of alcohol during the filling of a lamp or rupture of a bottle. Even more dreadful were those caused by the inflammation of ether. In November 1830, while Boullay was carrying on experiments with ether, the bottle broke in his hands near an open flame. The consequent explosion and fire caused him terrible burns, which left him in pain for several years and eventually led to his death.<sup>15</sup> His admission to the

*Société de Pharmacie* took place one week before his death [2].<sup>16</sup>

## SCIENTIFIC CONTRIBUTION

### Double chlorides and iodides

Boullay opened his first note<sup>8</sup> on the double iodides and chlorides pointing out that Jöns Jacob Berzelius (1779-1848) had distinguished between sulfur, oxygen, and other negative bodies on the ability of these elements to originate acids and bases by their combination with metals. If this property was particular to certain bodies, it certainly characterized in a clear-cut manner those who were so endowed. This was not the case for chlorine, iodine and fluorine [bromine was discovered in 1826 by Antoine-Jerôme Balard (1802-1876)]. The tendency of fluorides to join among themselves was well known. Boullay indicated that according to the experiments he had carried on under the guidance of Dumas, he had found that iodides and chlorides could equally give place to combinations, somewhat less stable, but having well pronounced characters. He had delivered to the *Académie des Sciences* samples of the combinations of mercury iodide, lead iodide and silver iodide, with potassium iodide. These combinations, and many other analogues between the iodides of negative metals and the iodides of positive metals, had the faculty of crystallizing when their solutions were concentrated, but they did it promptly upon addition of water, with deposition of the insoluble iodide. These same negative iodides were susceptible of uniting with alkaline chlorides under certain conditions, but the combinations were less stable and decomposed very easily. In this case the insoluble iodide precipitated in crystalline form. Finally, the chlorides also combined between them. Boullay gave as example the chlorides of silver, antimony, copper, and the alkaline chlorides.

Boullay wrote that he was carrying on the analysis of these many and diverse compounds, trying to determine experimentally the characteristics of these new acids and bases, considered within the limit of the ratios under which these reactions took place. He presented part of his findings in a following paper<sup>3</sup> referring in particular to double iodides. According to Boullay, when oxygen combined with a body, the resulting compounds had a basic or an acid tendency. The union of an acid and a base yielded salts, or less well defined. Under this viewpoint, chlorides, iodides, and sulfides were not salts but theoretically they resembled oxides and acids and their combinations gave birth to salts totally comparable to those of oxygenated bases and acids. The only difference consisted in that in the latter oxygen was their common electro negative principle while in the former it was sulfur, chlorine, and iodine. The purpose of this memoir was to extend the well-known method of combination of this well-known gender for the cyanides, fluorides, and sulfides, to bodies that Berzelius had put outside the series, that is, the iodides and perhaps chlorides.

His experimental results were as follows: (a) Combinations of hydrogen iodide with mercury iodide: hot hydrogen iodide dissolved mercury iodide and formed a compound containing two atoms (molecules) of acid and

one atom of iodide. Addition of water separated one part of iodide and the liquid now contained four atoms of acid and one atom of iodide. If instead of adding water to the hot solution, it was left alone, resulted in precipitation of crystallized mercury iodide, which after a short turned into yellow crystals while water separated from the pure insoluble iodide. Since the salt with two atoms of acid existed only when hot, and that of four atoms was soluble, it was very probable that the one in question was an intermediate compound containing three atoms of acid and one atom of iodide.

A solution of hot mercury iodide in hydrogen iodide in contact with dry air under slightly low pressure deposited long yellow transparent prisms, which decomposed into mercury iodide and hydrogen iodide. The acid remained gaseous if the air was dry but dissolved if it was humid. Hydrogen chloride behaved in a similar manner.

(b) Double iodides of mercury: Boullay found three series of salts of this gender, all contained the deuto iodide of mercury ( $HgI$ ) acting as an acid and combined with the iodides of potassium, sodium, barium, strontium, calcium, magnesium, and zinc. Salts of the first series were obtained by dissolving the hot deuto iodide in excess in a saturated solution of soluble iodide. The composition of all salts of this series was one atom of electropositive iodide and three atoms of mercury iodide. Cooling of the solution precipitated crystalline mercury iodide and a liquid containing one atom of electropositive iodide and two atoms of mercury iodide. All these iodides were extremely sensitive; they decomposed by simple drying.

(c) Ammonium iodide and mercury diiodide: Dissolving in hot mercury iodide in ammonium iodide produced a salt containing three atoms of mercury iodide and four atoms of ammonium iodide. Cooling deposited the excess of iodide and produced a salt containing two atoms of mercury iodide and one atom of ammonium iodide, which was very similar to the potassium salt. (d) Double iodide of mercury: This salt, composed of proto iodide ( $Hg_2I_2$ ) and deuto iodide ( $HgI_2$ ) of mercury, formed during specific circumstances of the precipitation or mercury salts by potassium iodide. When precipitating slightly acid mercury proto nitrate with potassium iodide, or when treating under heat mercury proto chloride with potassium iodide, a green precipitate of proto iodide formed. With an excess of alkaline iodide the mercury proto iodide decomposed into mercury, that separated, and deuto iodide that dissolved. (e) Combination of chlorides and iodides: Negative iodides combined with positive chlorides to form unstable combinations. Potassium chloride and ammonium chloride dissolved the deuto iodide of mercury under heat and decomposed mercury proto iodide, which precipitated and the deuto iodide, which dissolved. Hydrogen chloride also dissolved the deuto iodide. (f) Double iodide of lead and potassium; There were two salts of this gender, the first composed of one atom of potassium iodide and two atoms of lead iodide, and the second by one atom of potassium iodide and one atom of lead iodide. The first was obtained by mixing in the cold a concentrated solution of both iodides; the second by mixing lead iodide with an excess of a concentrated solution of potassium iodide. (g) Double

**Note 2.** Félix Boudet read the report about the admission of Félix Polydore Boullay. A vote was held and M. Boullay was admitted by unanimity.

The *Société de Pharmacie* did not rejoice for long on counting Polydore Boullay as one of its members; Polydore Boullay, admitted on May 16, passed away on May 23...<sup>16</sup>

iodide of tin: Boullay studied the double iodides of tin, potassium, sodium, barium, strontium, and ammonia. They were obtained by mixing solution of tin protochloride,  $\text{SnCl}_2$ , and potassium iodide. (h) Double iodide of silver and potassium. There were two salts of this gender, one neutral and the other basic. The first was contained one atom of alkaline iodide and one atom of silver iodide, the second, two atoms of potassium iodide and one atom of silver iodide.

### Etherification

According to Dumas and Boullay<sup>9</sup> the reaction between alcohol and concentrated sulfuric acid gave place to different substances depending on the operating conditions. The properties of the products were so different that they believed the reaction should be studied in more detail. A few years before Fourcroy and Vauquelin<sup>17</sup> had proposed a theory about the formation of sulfuric ether, which seemed to be solidly established. They believed that when alcohol was contacted with sulfuric acid, the latter removed part of the water of the former and transformed it into ether. Towards the end of the reaction, when the alcohol had become less abundant and the temperature was higher, a new reaction took place generating sulfur dioxide and sweet wine oil. Later, Dabit reported the formation of a particular acid during etherification (sulfovinic acid).<sup>18</sup> Fourcroy and Vauquelin's theory, simple and complete, had been supported by the experiments of Nicolas Théodore de Saussure (1767-1845),<sup>19</sup> who demonstrated that the same as alcohol, the sulfuric ether was also formed from carbon, hydrogen, and oxygen in the necessary proportions to conform water and dicarbonated hydrogen (gas oléifiant, ethylene,  $\text{C}_2\text{H}_4$ ). Saussure also proved that ether contained less water than alcohol. Afterwards, Joseph-Louis Gay-Lussac (1778-1850) used the value of the densities of the vapors of water and the ether to reach the same conclusion.<sup>20</sup> He showed that alcohol had to be formed by equal volumes of water vapor and dicarbonated hydrogen while sulfuric ether had to contain two volumes of dicarbonated hydrogen per one volume of water vapor. The reaction between alcohol and sulfuric acid led to the formation of sulfuric ether (alcohol deprived of one half of its water), a sweet wine oil of unknown composition, and hyposulfuric acid, accompanying the latter and of unknown composition. All these results were confirmed by other scientists and seemed to overthrow Fourcroy and Vauquelin's theory. Dumas and Boullay believed that the only way to find the correct interpretation was to make a very precise analysis of all the reagents and products of the reaction. Very careful purification of the alcohol and chemical analysis of the same confirmed beyond doubt that it was formed by one volume of dicarbonated hydrogen and one volume of water vapor ( $\text{C}_2\text{H}_4 + \text{H}_2\text{O}$ , that is,  $\text{C}_2\text{H}_6\text{O}$ ). Afterwards, Dumas and Boullay synthesized sulfuric ether and distilled it over calcium chloride until its properties remained unchanged. They reported it had a density of 0.713 at 20 °C and a boiling point of 34 °C at 745 mmHg. Chemical analysis indicated that it contained one volume of dicarbonated hydrogen and a half a volume of water vapor ( $2\text{C}_2\text{H}_4 + \text{H}_2\text{O}$ , that is,  $\text{C}_4\text{H}_{10}\text{O}$ ). The sweet oil of wine was separated from pure ether by distillation and then rectified over calcium chloride and KOH. Its density was found to be 0.917 4 at 10.5 °C and to contain four volumes of carbon and three volumes of hydrogen,  $\text{C}_2\text{H}_3$ , a simple composition and very different from all known hydrocarbons. The next stage was the analysis of barium sulfovinatate (sulfovinic

acid = ethyl hydrogen sulfate). The chemical analysis of the oily matter gave exactly the same composition as that of the sweet oil of wine, that is, 88.37 % carbon and 11.63 % hydrogen. A similar conclusion was obtained after analyzing the sulfovinates of copper and of lead, proving that the composition of the oil present in the sulfovinates was exactly that of sweet oil of wine. All these results led Dumas and Boullay to propose their theory of the etherification reaction: During the reaction the acid and the alcohol split into two parts, one containing the sweet oil and hyposulfuric acid and the other, the ether and diluted acid. This mechanism served also to explain the role played by manganese dioxide or chromic acid in the process of etherification: they lost part of their oxygen to form water and the sweet oil and thus prevented the formation of hyposulfuric acid.

In a following publication Dumas and Boullay<sup>10</sup> reported their results on the preparation of esters (then named ethers), which they defined as compounds formed from an alcohol and an oxygenated acid (inorganic or organic). In particular, they prepared ethyl nitrate, ethyl acetate, ethyl benzoate, and ethyl oxalate and compared their results with those obtained by Louis-Jacques Thenard (1777-1857).<sup>21</sup> Thenard had reported that treatment of these esters with pure KOH transformed them, rather easily, into potassium hyponitrite, acetate, benzoate, or oxalate, respectively, and alcohol. From this result he concluded that esters were formed from the acids contained in the potassium salts and the alcohol that was liberated, in other words, esters were true salts where the alcohol functioned as the base. Nevertheless, the elemental analysis of the esters did not agree with this line of thought. Oxalic ester, for example, contained the same amount of carbon than the alcohol, although oxalic acid contained less; ethyl acetate contained more carbon than the alcohol, although acetic acid was less richer in carbon than the alcohol. Dumas and Boullay were surprised by this discordance and looked into its possible causes. Again, their first step was to check the purity and composition of the starting materials, (alcohol, acetic acid, benzoic acid, and oxalic acid). They found them to be identical to that reported by the best sources. Hence, they started from the hypothesis that the combined esters they were examining were actually formed from an oxygenated acid and sulfuric ether (diethyl ether). Withdrawal of the alcohol by means of KOH led the nascent ether to grab the water necessary to return to the alcohol state. To test their hypothesis they examined the esters from three different viewpoints. First, they determined their elemental composition, then they measured the density of the vapor, and finally, they made a direct determination of the amounts of alcohol and acid formed.

The memoir gave a detailed description of the synthesis procedure used for each ester and the results of their elemental analysis carried on by passing the vapors over copper oxide heated red. For the hyponitrite they obtained four volumes of  $\text{CO}_2$  per volume of nitrogen, representing the elemental composition (% vol.): carbon 32.02; nitrogen 18.83; hydrogen 6.65, and oxygen 42.50, that is, ethyl nitrate could be assumed to be formed of one volume of ether and one volume of hyponitrous acid. For ethyl acetate, the results were carbon 54.65; oxygen 36.28; and hydrogen 9.07, that is, ethyl acetate could be represented by one atom (mole) of sulfuric ether,  $\text{C}_8\text{OH}_{10}$  and one atom of acetic acid,  $\text{C}_8\text{H}_6\text{O}_3$ . For ethyl benzoate the results were carbon 73.32; oxygen 19.10; and hydrogen 7.87, that is, it could be represented by one atom

(mole) of benzoic acid,  $C_{30}H_{12}O_3$  plus one atom of sulfuric ether,  $C_8H_{10}O$ . For ethyl oxalate the results were carbon 49.42; oxygen 43.75; and hydrogen 6.83, that is, it could be represented by one atom (mole) of oxalic acid,  $C_4O_3$  plus one atom of sulfuric ether,  $C_8H_{10}O$ .

The vapor density measurements were confronted against the different possible compositions (the values were reported against the density of air assumed to be 1). For example, for ethyl nitrate the average of three measurements gave a density of 2.636. Assuming the ester to be formed by alcohol and hyponitrous acid, no hypothesis could satisfy simultaneously the results of the elemental analysis and the density of the vapor. On the other hand, assuming that the ester was formed by sulfuric ether and hyponitrous acid, in the proportions given above, then the calculated density was 2.627, which compared very favorably with the experimental data. A similar conclusion was obtained for the other three esters studied.

From the above description, it can be seen that the difference of Dumas and Boullay's mechanism against the ones suggested by others, was on the role played by water. Dumas and Boullay showed that the water disappeared. They believed ether to be a salifiable base and alcohol an ether hydrate; the esters ethyl nitrate, ethyl acetate, ethyl benzoate, and ethyl oxalate were formed of ether and acid. The esters differed from the alcohol in that water vapor replaced an equal volume of liquid water. From the viewpoint of radicals, they concluded that dicarbonated hydrogen had a powerful power of combination comparable to that of ammonia, an anhydrous alkaline gas. To substantiate their claim, Dumas and Boullay synthesized and analyzed a large number of ammonia compounds and put into evidence the parallelism that existed between them and those of dicarbonated hydrogen. A sequel of this work was the discovery of amides and nitriles, the dehydrated products of the former.

Dumas and Boullay concluded that dicarbonated hydrogen played the role of a powerful alkali, having a saturation (neutralization) capacity identical to that of ammonia, and open to many reactions and properties, such as solubility in water; alcohol and sulfuric ether were the hydrates of dicarbonated hydrogen; and compound esters were the salts of dicarbonated hydrogen. These salts were anhydrous when formed from haloacids, and hydrated when formed from oxacids; many acids seemed to form double salts with dicarbonated hydrogen, corresponding to sulfovinic acid (ethyl sulfate). These acids salts united to bases yielded double salts, analog to sulfovinates; nascent ether could subsequently transform into alcohol under diverse influences that made it absorb water or lose dicarbonated hydrogen; there was a clear similarity between fatty materials and esters, and finally, sugar cane and raisin sugar could be considered as composed of  $CO_2$ , dicarbonated hydrogen, and water. Similarly, sugar cane could be considered the carbonate of sulfuric ether and raisin sugar (glucose) the carbonate of alcohol. Dumas and Boullay wrote that cane sugar had to be considered formed by one atom of ether vapor and two atoms of carbonic acid ( $C_4H_{10}O + 2CO_2$ ) and sugar raisin (glucose) and starch, by one atom of alcohol plus one atom of carbon dioxide ( $C_2H_6O + CO_2$ ). In other words, cane sugar and starch were considered to the carbonates of hydrogen dicarbonated, differing only on the amount of water they contained.

Dumas and Boullay's theory of etherification was thoroughly discussed by Jöns Jacob Berzelius (1779-1848) in his annual chemical review (Jahresbericht) for 1828.<sup>22</sup>

According to Berzelius the theory must be regarded as an attempt "to understand the mutual proportions of the elements by attaching them to the formulae of other well known compositions". Four years later<sup>23</sup> Berzelius proposed the name "etherin" (Aetherin) for  $C_2H_4$  and the name was afterwards also used for Dumas and Boullay's theory.<sup>24</sup>

Alexander William Williamson (1824-1904) would eventually unveil the correct mechanism of the etherification reaction.<sup>25,26</sup>

### The volume of atoms

The opening statements of Boullay's thesis in chemistry<sup>4</sup> are interesting because they give a good picture of the knowledge and ideas about the structure of matter, which were prevalent in 1830. The concepts of atom and molecules were then used loosely and not necessarily expressed the meaning they have today: "The knowledge of the intimate structure of bodies is one of the most interesting questions that has occupied the minds of physicists and chemists and given place to many hypotheses. Do we admit the possibility of an unlimited division of matter or that of its stopping at particles infinitely small that no mechanical force can further divide them? These extreme molecules that resist mechanical efforts, will they also resist chemical forces or will they be able to divide further in order to combine with other molecules or their fractions? Is matter continuous or is it composed of particles separated by empty space having a volume largely exceeding that of the elementary particles? What is the shape of these particles; is it different for each one of them, or is it different only for certain groups of these substances? Is the nature of these elemental molecules uniform or different? Finally, which forces connect the molecules together; are they of a physical nature, linking two similar molecules, and which can, perhaps, be assimilated to the mechanical forces of pressure or traction, or chemical forces, that link two molecules of different nature, and having no analogy to the forces acting in mechanics? One of these many questions has caught my attention, not only because of its importance but because it has been the source of some many risky ideas that I believe should pointed out and destroyed. I am talking about the determination of the probable volume of the atoms of simple bodies in the same state of aggregation, and the modifications that it can experience in chemical combinations."

Boullay believed that one of the parameters for this determination was the specific gravity of the bodies. First of all, it was necessary to evaluate the information available, verify its trustfulness, and complement it with new measurements to fill the many gaps existent in the tables. Boullay then explained that the specific gravity of a substance should be measured in a well-crystallized state or grossly pulverized. If the crystals presented empty spaces it was enough to break them into much smaller crystals, which could then be considered as sufficiently pure. If the material did not crystallize it was necessary to pulverize it to a fine powder by mechanical means or by chemical precipitation. The results were always the same if the proper precautions were taken; the procedure for crystalline bodies was easy because it was enough to determine the weight of the material in air and in water. In the case of pulverized materials it was necessary to eliminate the adhered air by prolonged vacuum.

Boullay presented a table giving the value of the specific gravity, reported in the literature or measured by him, of a very large number of elements, several of

their oxides, and many salts. He then analyzed the results from two viewpoints:

(a) **Simple bodies**

This was the easiest situation because the bodies could be assumed to be formed by similar molecules, separated one from the other by the same distance, probably very large in comparison to their volumes. One question was how to establish the relation existing between the volumes of two atoms belonging to simple bodies of very different nature. If matter was continuous, the problem did not present any difficulty as long as the density of atomic weight of the two bodies was known: the ratio between these two properties would give the required volumes. Thus, for sulfur having specific gravity 2.086 and atomic weight 201.160, the atomic volume would be  $201.16/2.086 = 96.430$ , and for iodine, it would be  $783.35/4.948 = 158.300$ , and the ratio of the relative volumes would then be 158/96, that is, about 5 to 3.

Now, admitting, as done in the prevailing hypotheses, that the molecules were separated by large empty spaces, it was impossible to conclude anything regarding their proper volume, which depended not so much on the total volume density of the substance, but also on their proper density, which remained unknown. In the existing situation it was necessary to make additional hypotheses and to see how to modify the ideas regarding the composition of the bodies, for example, to add to each molecule the surrounding volume and thus form continuous elements. These volumes became very appreciable and were given by the ratio of the weight of the atom to the specific density of the body from which they formed part. This hypothesis led to a table reporting the value of the atomic sphere of 26 elements.

(b) **Compound atoms**

Here the situation was much more complicated. Assuming, for example, that the substance in question was lead sulfide and that the combination contained an equal number of molecules of sulfur and the metal, then, calling  $V$ ,  $V'$ , and  $V^s$  the volumes of the atomic sphere of sulfur, lead, and lead sulfide, respectively, there were two possibilities: (1)  $V^s = V + V'$  and (2)  $V^s$  larger/smaller than  $V + V'$  ( $V^s$  could be easily calculated from the weight and density of the sulfide). Boullay reported his results for several sulfides (antimony, mercury, lead, arsenic, tin, silver, and iron) and chlorides (silver, mercury, lead, and potassium). The results indicated that the sulfides contracted while for chlorides expanded.

Boullay then proceeded to calculate the atomic volume of oxygen and chlorine, using the data available for a large number of oxides and chloride. Examination of the results indicated that the calculated atomic volume of oxygen varied extremely, (between 17 and 79) a result indicating large contraction or dilation effects. The results for chlorine were even more prominent; it was seen that the atomic volume of potassium chloride was smaller than that of potassium, a result indicating an enormous contraction, which was undoubtedly due to the large affinity of chlorine for potassium.

The general results indicated that on view of the present state of knowledge, it would be erroneous to try to get even an approximate idea of the volume in the solid state of the atoms of substances such as oxygen and chlorine, which had not yet been reduced to that state.

Boullay now tried to find if there was a relation between atomic volumes and the forces of cohesion and chemical affinity. Cohesion forces were those that united the similar molecules that compose a given body. This force, which could be overcome by mechanical actions,

could also be overcome by heat. Regrettably, there were only vague ideas regarding this force and even more about how to evaluate it. It was well known that many properties depended on it, for example, hardness, malleability, ductility, and tenacity, but regrettably most bodies possessed only part of these faculties; some of them were very hard and nevertheless were broken by the slightest shocks; others could be easily laminated but not drawn. Meanwhile, there was some agreement that the action of a metallic file could offer an approximate measure of the cohesion force. Although this essay could not be quantified it offered a tool for classifying bodies, with a high degree of uncertainty for those presenting similar results, and great possibilities for others, which were widely separated (by the action of the file).

Suspecting that the substances with the greatest cohesion should have their molecules the closest together, Boullay drew a table in which he arranged the simple substances in a progressive series: the first position corresponded to the substance with the smallest atomic volume, and the last, by the one with the largest atomic volume. The tabulated value demonstrated that his conjecture was not unfounded. In fact, in the first position was found carbon, the hardest of all substances, and in the last position sodium and potassium, which are the softest.

Encouraged by his findings, Boullay decided to extend his work to compound bodies, with the understanding that here he had to take into account an additional force, chemical affinity. As a first example he considered again lead sulfide; the volume of the binary molecule should depend both on the affinity of sulfur for lead and on the cohesion of the sulfide molecules. On the one hand, the larger the chemical affinity of lead for sulfur, the more the two molecules of the two compounds would approach each other, with the corresponding decrease in the atomic volume. On the other hand, the larger the cohesion of the sulfide molecules the more the binary molecules would approach each other and the atomic volume of the sulfide would be smaller. Boullay repeated that by atomic volume he assumed that of the material molecule plus a certain portion of the surrounding volume. Accordingly, for a series of analog bodies, the one having the largest cohesion and the largest affinity should present the largest contraction in the atomic volume.

Boullay gave the following examples that confirmed or weakened the preceding hypothesis: (1) the results for sulfides seemed to support the hypothesis. Iron persulfide,  $\text{FeS}_2$ , presented the largest contraction in atomic volume, that resulted from a very large chemical affinity and a very large cohesion. Silver sulfide, which was ductile and malleable, and hence had a large cohesion, was the result of a powerful affinity between silver and sulfur. Then came, with a weaker contraction, the sulfides of tin, arsenic, lead, mercury, and antimony, and this order seemed to be in harmony with the decrease in chemical affinity and cohesion of these compounds; (2), the iodides, offered a notorious verification of the same ideas. Potassium iodide presented a large condensation in the volume of its atom, while the other iodides yielded an expansion, a difference that agreed perfectly well with what was known about the predominant affinity of iodine for potassium; (3) the chlorides also confirmed the hypotheses: The volume of potassium chloride was smaller than that of potassium. Now, the cohesion of the compound was considerable and resulted in one of the strongest chemical combinations known. The volume of

sodium chloride was not very much larger than that of the metal. It was also seen that there was a sizable contraction of the elements of silver chloride, when compared to that of mercury chlorides, facts, which attested well with the well-known affinity of chlorine for silver. To these observations it could be added that although silver chlorides experimented a contraction in comparison with mercury chloride, silver iodide compared to the iodides of mercury, presented a dilation, and this result was justified by the difference existing between the cohesion of both compounds. The one of silver chloride appeared larger because it was elastic, it hardly broke and strongly resisted the action of the voltaic cell, while a minimal pressure reduced silver iodide to a powder; (4) the results obtained with oxides also substantiated the assumed hypotheses. It was seen, taking the extreme points of the series, that the oxides, which offered the most significant volume, the largest dilation and the less condensation among the elements, were silver oxide and cuprous oxide, which resulted from a less powerful affinities, while the oxides of tin, antimony, which resulted from very strong affinities, were the ones presenting a considerable contraction.

Boullay summarized his findings as follows: (1) In chemical combinations, the atomic volume of the compound was usually much larger or much smaller than the sum of the atomic volumes of the composing elements, that is, there was contraction or dilation, (2) the contractions observed were sometimes quite considerable, and the atomic volume of the compound was smaller than the atomic volume of one of the components, (3) in the present state of knowledge, it was not possible to estimate the volume in the solid state of substances such as oxygen and chlorine, which had to be brought yet into that state, (5) in the simple substances there was an apparent relationship between the cohesion and the volume of atoms, so that the greatest cohesion corresponded to the smallest volume, (6) with compound bodies, it was observed that within certain series of compounds, the smallest atomic volumes corresponded to the largest cohesion of the compound and the largest chemical affinity between the components.

### Ulmine

Boullay's second doctoral thesis was related to vegetable chemistry.<sup>5</sup> According to Boullay, the numerous circumstances that originate ulmine and the consequences that result from the constant day-to-day transformation of a multitude of vegetable matter, under a wide range of influences, those of woods in particular, its presence in vegetable earths, manure, sap, etc., were a clear proof of the important role it plays in nature. Ulmine seemed to be one of the most valuable known fertilizers, probably the fertilizer by excellence. It was available in very large deposits on bole, compost, heath peat, peat moss, etc. etc. It was thanks to their peat bog that Holland enjoyed such superiority in their agricultural products.

In this thesis Boullay first recalled the information available about the discovery of ulmic acid in the exudation products of the elm tree [3], its artificial manufacture, its finding in soot, in the ground, in peat, in the coloring matter of raw flax, in the products resulting from the action of sulfuric acid on vegetable matter, in the products of the distillation of wood, in fumes, in powders, etc., then described its properties, proved that it was different from the products of the action of oxygenated materials on the extracts of gallic acid, described the diverse combinations of the acid, and finally entered into a detailed description of the material he named azulmic acid: It was insoluble in cold and hot water, in cold and hot alcohol, but it dissolved in cold concentrated nitric acid yielding a light pink solution.

Louis Nicolas Vauquelin (1763-1829) had discovered ulmine in the exudations of old sick elm trees, characterized it, and gave it its name (from elm = *ulmus*, the Latin name of the tree).<sup>27</sup> Henri Braconnot (1780-1855) found that treating different ligneous materials with sulfuric acid converted them first into gums and then into sugars and a particular acid (which he named *vegeto-sulfuric acid*).<sup>28</sup> Heating a ligneous material with an equal weight of KOH and a small amount of water resulted in the softening, swelling, and almost instantaneous dissolution of the wooden fraction. The final mixture dissolved easily in water giving a brown liquid, without leaving much of a residue. Addition of an acid yielded an abundant brown precipitate, which in the dry state had a brilliant black color and all the properties of ulmine (which Braconnot named artificial ulmine). Treatment of wood sawdust by the same procedure converted about 25 % of it into ulmine. Braconnot indicated that he had found ulmine in many aging products of the plant world. He considered the soluble part of certain composts to be formed by ulmine and ammonia. Braconnot also found that soot contained ulmic acid in large amounts. According to him, dry ulmine was a black solid, very fragile; its broken pieces were vitreous and had the brightness of jet black, it was almost tasteless, had no smell, and was insoluble in cold water. It dissolved in hot water, producing a coffee-like solution, which was precipitated by the nitrates of mercury and lead, leaving a colorless liquid. Other salts, such as iron sulfate, barium nitrate, aluminum acetate, sodium chloride, and calcium chloride, also precipitated it, but after some time. Ulmine was very soluble in alcohol and concentrated sulfuric acid, it dissolved in hot acetic acid and water precipitated it from all these solutions. It neutralized completely NaOH, KOH, and ammonia, and tinted litmus paper blue. Acids precipitated ulmic acid as a flocculent red brown powder, insoluble in cold water, slightly soluble in hot water. Calcareous and metallic earths, limewater, cast iron, etc., also produced precipitates.<sup>28</sup>

Since ulmine formed salts with salifiable bases and saturated alkalis, Boullay believed it was better to call it ulmic acid. Boullay analyzed ulmic acid and reported that it contained 56.7 % carbon and 43.3 % water, while

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**Note 3.** Dutch elm disease is caused by the vascular wilt ascomycete microfungus, *Ophiostoma ulmi* (formerly *Ceratocystis ulmi*), carried from diseased trees to healthy trees via elm bark beetles. Affected trees develop a brown discoloration in the water conducting vessels (xylem) of the wood. In an attempt to block the fungus from spreading further, the tree reacts to its presence by plugging its own xylem tissue with gum and tyloses, bladder-like extensions of the xylem cell wall. As the xylem delivers water and nutrients to the rest of the plant, these plugs prevent them from traveling up the trunk of the tree, eventually killing it. Eventually, the roots die, starved of nutrients from the leaves. Cerato-ulmin, a toxin involved in Dutch elm disease, has the structural features of fungal hydrophobins, the components of microbial cell walls that contribute to cell surface hydrophobicity.

gallic acid had 57.08 % carbon and 42.92 % water corresponding to the formula  $C_6H_6O_3$  (assuming C = 75.33), which seemed to indicate that ulmic acid and gallic acid differed only in the crystallization water. Boullay prepared a series of insoluble ulmates (e.g. silver, lead, copper) and from their analysis deduced that the molecular weight of ulmic acid was 3 682.34, corresponding to the formula  $C_{28}H_{28}O_{14}$  (assuming C = 75.33). The analysis of copper ulmate led to the molecular weight of 3 945.44 for ulmic acid, that is,  $C_{30}H_{30}O_{15}$ , which Boullay believed to be more accurate. Hence the ratio of molecular weight between ulmic acid and gallic acid was 5 : 1.

The action of concentrated sulfuric acid on sugar cane was known to be very energetic. The material browned almost immediately and then carbonized. It was possible to get a small amount of ulmic acid from the residue. Although it was not recommended to use HCl because the reaction was very impetuous, using heat and diluted HCl converted cane sugar into a material containing a substantial amount of a brown material, very similar to ulmic acid. Treating sugar cane with cold diluted sulfuric acid transformed the raw material after some time into raisin sugar (glucose), which was not attacked by concentrated sulfuric acid.

Treating raisin sugar with a hot alkaline base turned it colored little by little and yielded a brown liquor from which addition of an acid precipitated a brown flocculent material that seemed to be ulmic acid. Cane sugar, under the same conditions, was not colored and did not seem to suffer any alteration, even after many hours under the action of the base. These opposing actions of the same agents on two sugar species seemed peculiar and showed that these materials presented fundamental differences in their constitutions, which seemed to derive from the presence of one more mole of water.

Ulmic acid seemed to be different from the product resulting from the action of air or oxygenated agents on the extracts, on tannin, and on gallic acid and gallates, because of its color and solubility in alcohol. Hence it should be differentiated with these bodies with whom it was usually confused.

Consideration of the numerous circumstances under which ulmic acid presented itself, and the fact that it was one of the common products of the decomposition of vegetable matter, slow and spontaneous, or fast under energetic agents, led to the question if under similar circumstances, animal matter would generate a compound similar to ulmic acid. Boullay believed that the answer to the question was positive. Actually, there was a nitrogen material quite analogous to ulmic acid by its physical and chemical properties, which originated from more than one chemical reaction; it was the carbonaceous substance resulting from the spontaneous decomposition of pure hydrogen cyanide. Boullay made a chemical analysis of this carbonaceous substance and studied all its properties in the same way he had studied ulmic acid.

Boullay summarized his findings as follows: (1) The ulmine discovered by Vauquelin in the exudation products of the elm tree, and afterwards found in bole and compost, and prepared artificially by Braconnot, was also present on crude flax (were it formed the forming coloring matter), in the distillation products of wood, in soot, in vegetable matter incompletely distilled, such as

smoke, and consequently in Bouchet's powder. It was also one of the ordinary products of the action of sulfuric or hydrochloric acids on vegetable matter such as wood, starch, cane sugar, and alcohol. It was generated by the action of bases on raisin sugar (glucose) and amyloseous lignin; (2) considering the properties of ulmine, it seemed better to change its name to ulmic acid. Ulmic acid appeared to be different from the product obtained from the action of air or oxygenated substances on tannin, gallic acid, and gallates, on its color and solubility in alcohol, (3) ulmic acid had the same composition as gallic acid, but a weaker neutralizing power. Analysis of their salts indicated that the ratio between the molecular weights of ulmic acid and gallic acid was 5 : 1. The weak neutralizing ability of this acid, which seemed to be an excellent fertilizer, indicated that it could be transferred to plants with the aid of a very small amount of an alkaline base, (4) in spite of the analogy between ulmic acid and gallic acid, it was not possible to transform the latter into ulmic acid with the aid of sulfuric acid. The product of such a reaction seemed to be similar to the one resulting from the action of oxygenated substances on gallic acid and extracts, (5) the carbonaceous material resulting from the spontaneous decomposition of hydrogen cyanide, did not seem to be a nitrogen derivative of carbon, as supposed by Gay-Lussac, but rather a hydrogenated compound capable of combining with salifiable salts, similar to hydrogen cyanide itself, (6) the same compound seemed to be produced when animal matter was subject to a reaction similar to those which transformed vegetable matter into ulmic acid (for example, the action of KOH on gelatin). Based on the similarity of physical and chemical properties of these two substances, it seemed more appropriate to name the latter azulmic acid, a name that expressed the difference in their chemical nature [4], (7) azulmic acid was produced not only by the spontaneous decomposition of hydrogen cyanide, but also by that of ammonium cyanide, cyanides dissolved in water, and by the reaction of the gas with bases; in short, it was found whenever we dealt with cyanogen compounds, (8) the spontaneous decomposition of pure hydrogen cyanide seemed to transform it into ammonium cyanide and carbon dioxide, a result completely in accord with the analysis of azulmic acid, (9) the action of diluted nitric acid upon cast iron, that is, over the finely divided carbon it contains, generated a nitrogenous substance possessing the main properties of azulmic acid, and (10) azulmic acid appeared to combine with concentrated nitric acid, which dissolved it. This result seemed to indicate to believe that artificial tannins were simply a combination of this compound with nitric acid, or at least, a similar product.

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**Note 4.** A prevalent French name for nitrogen was azote, symbol Az. For this reason Boullay added the prefix az to ulmic acid to indicate it was an nitrogenated derivative.

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